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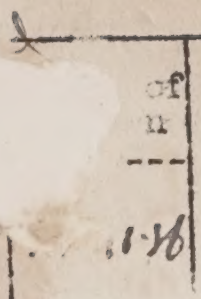

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IN
CHEMICAL ENGINEERING

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CHEMICAL ENGINEERING SERIES

APPLIED MATHEMATICS IN CHEMICAL ENGINEERING

BY

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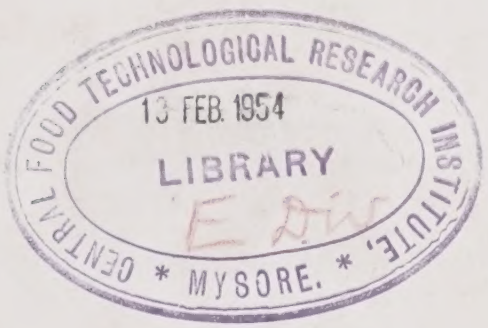

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PREFACE

Chemical engineering gives many indications of rapid advancement along quantitative and mathematical lines. Paralleling the early development of civil and electrical engineering, the accumulation of basic theories and empirical data is being followed by the development of the mathematical techniques of using this information to the greatest advantage in practice. These mathematical techniques will assume an increasing importance in the future, and the engineer without an adequate mathematical background will find himself under an even greater handicap than at the present time.

It is already evident that the undergraduate courses in differential and integral calculus are inadequate as a basis for following the current literature both in applied chemistry and in the unit operations. Beyond the basic calculus, the chemical engineer's needs are rather specific; his primary needs are a facility in analyzing problems with the help of differential equations, and a familiarity with the many useful graphical methods. The usual course in advanced calculus includes many proofs of theorems which he is willing to take for granted, and includes topics, such as vector analysis, for which he finds little application in his work. The courses and texts on differential equations are usually excellent in their handling of the problem of solving a differential equation, but of little help in the equally important problem of setting up a differential equation to express a physical or chemical problem. It is hoped that the present book, written by chemical engineers who do not pretend to be mathematicians, will prove helpful to those who have found books on applied mathematics written by mathematicians to be unsatisfactory, and that it may be of sufficient practical use to offset its deficiencies from the mathematician's point of view.

Following an introductory review, Chaps. II and III are devoted to the problems of setting up and solving ordinary differential equations. Facility in setting up differential equations to express a physical situation is best achieved by studying practical examples, and the various illustrative problems form an integral part of the text. Chapter IV treats partial differentiation, with special reference to the handling of partial differential coefficients encountered in thermodynamics. Chap-

ters V and VI deal with infinite series and their use in the solution of ordinary and partial differential equations. An attempt has been made to make the treatment of Fourier series and Bessel functions as simple and practical as possible, with a number of illustrative problems in heat conduction and diffusion. The ingenious Schmidt method of handling problems in heat conduction, apparently not widely known in this country, is illustrated with several examples. Chapter VII describes methods of fitting data by empirical equations, numerical integration, interpolation, and numerical differentiation. Chapter VIII presents illustrative examples of the many valuable graphical methods finding widespread use in chemical engineering design and a short section on alignment charts. Chapter IX discusses errors and the precision of measurements. Because of the variety of problems discussed, the book may be regarded as being a treatment of chemical engineering as well as of mathematics, although the arrangement of subject matter is based on the mathematics. A discussion of dimensional analysis is omitted, because this subject is treated in Perry's "Chemical Engineers' Handbook" and in Walker, Lewis, McAdams, and Gilliland's "Principles of Chemical Engineering."

It should be possible for anyone with a good grounding in calculus to follow the text without great difficulty. It should be recognized, however, that there is no quick and easy method of gaining a proficiency in any branch of mathematics, and the student should expect to have to make a serious and concentrated effort to study the problems carefully if he is to find the book of help.

Thanks are due Prof. R. D. Douglass, for his cooperative help in connection with several points, and Prof. W. G. Whitman, for his critical review of Chap. IX. Several of the illustrative problems have been supplied by Dr. L. A. Monroe and J. E. Seebold. References are given to sources of data used in illustrative problems, etc., but no attempt has been made to give detailed references to the various standard texts on mathematics. Of the latter, Woods's "Advanced Calculus," Lipka's "Graphical and Mechanical Computation," and Scarborough's "Numerical Mathematical Analysis" have proved especially helpful.

Cambridge, Mass.,
January, 1939.

Thomas K. Sherwood,
Charles E. Reed.

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APPLIED MATHEMATICS IN CHEMICAL ENGINEERING

CHAPTER I

INTEGRATION AND DIFFERENTIATION

1. Introduction. The general concept of the rate of a reaction is of fundamental importance in almost all the various processes dealt with by the chemical engineer. It is the rate at which the reaction proceeds that determines the size of the equipment necessary for a specified performance or that determines the performance of a given apparatus. This is true not only in the case of chemical reactions but in the physical processes of heat transfer, diffusion, and flow of fluids, on which much of present-day chemical engineering is based.

Many of the generalizations constituting the basic laws of chemistry and physics applicable to chemical engineering are expressed in the form of differential equations, *i.e.*, they specify the rate at which the reaction or process takes place under conditions where the various important factors influencing the result are held constant. In the actual engineering operation, the controlling variables are seldom constant, and the allowance for the continual change in operating conditions represents a practical problem that confronts the chemical engineer. Many of the basic laws require much empirical information in the form of reaction-rate constants, heat-transfer coefficients, etc., in order to make them usable. In recent years, data and information of this type have been accumulated at an increasing rate; so it is now possible to apply the basic laws more broadly than ever before to the various engineering problems.

Perhaps a majority of the problems encountered deals with rate of change with time, as in batch operations, but it is also common for the important variable to be rate of change with position, concentration, etc. The basic law of fluid friction, for

example, specifies the variables affecting the rate of change of fluid head with respect to position in the conduit. In a continuous operation, as in a continuous-flow heat exchanger, the basic law specifies the rate at which heat transfer occurs at any point in the apparatus but leaves to the ingenuity of the engineer the problem of determining what happens in the apparatus as a whole. It is apparent that the answer to this latter problem should be obtainable by adding the results of what occurs at all the "points" in the apparatus, this addition constituting the process of integration. Because of the importance of the various rate equations in chemical engineering, the mathematical process of integration is a tool of special significance to the chemical engineer.

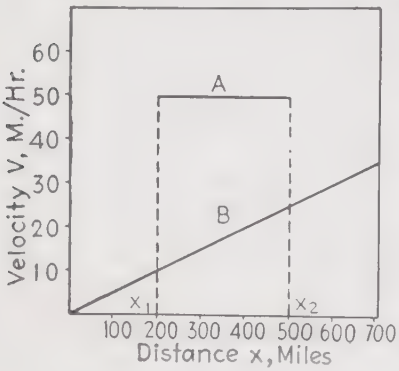


FIG. 1.

2. Integration. The process of integration is best understood by following a familiar problem with reference to a graph. Suppose a car is moving along a straight road at a constant velocity V. Let x represent the distance along the road in miles and θ represent the time in hours. The velocity V is represented by the derivative or differential coefficient $dx/d\theta$, which in this case is constant and equal to C as indicated by line A of Fig. 1. The time required to go from the 200- to the 500-mile point at a constant velocity of 50 m.p.h. is obviously

$$\frac{500 - 200}{50} = 6 \text{ hr.} = \frac{x_2 - x_1}{V} = \frac{x_2 - x_1}{dx/d\theta}$$

This calculation may be looked upon as summing up the short intervals of time for each of the 300 miles.

If the velocity is not constant, the case is more difficult. Assume V to be linear in x, *i.e.*, that the relation between velocity and distance may be represented by the straight line B of Fig. 1, whose equation is

$$V = \frac{dx}{d\theta} = 0.05x \tag{1}$$

The time required to go from the 200- to the 500-mile point may be calculated approximately by employing an average velocity.

such as the value 17.5 m.p.h. corresponding to the 350-mile point. The time would be

$$\frac{500 - 200}{17.5} = 17.13 \text{ hr.}$$

A somewhat better result would be obtained by adding the times for each 100 miles. The average velocity for the first 100 miles is 12.5 m.p.h. and the time 8 hr.; for the second hundred miles the average velocity is 17.5 m.p.h. and the time 5.71 hr.; for the last hundred miles the average velocity is 22.5 m.p.h. and the time 4.45 hr. The new value for the total time is 18.16 hr., or more than 1 hr. longer than the first value. As the 300-mile distance is broken up into a larger number of increments, the summation will give a more nearly correct value for the total time. The correct total time is obtained when the interval $x_2 - x_1$ of 300 miles is broken up into an infinite number of increments, and the time is obtained by adding an infinite number of time elements. This process is integration.

The differential element of time $d\theta$ required to traverse the differential distance dx is obtained by dividing dx by V, giving $dx/0.05x$. The total time is the summation of all these $d\theta$'s, expressed mathematically as

$$\theta_2 - \theta_1 = \int_{x_1}^{x_2} d\theta = \int_{x_1}^{x_2} \frac{dx}{0.05x} = 20 \int_{x_1}^{x_2} \frac{dx}{x} \tag{2}$$

The integral sign means "summation," the subscript and superscript indicating the values of x between which the summation is carried out. These limits of integration in this case are $x_1 = 200$ and $x_2 = 500$ miles. The value of $\int \frac{dx}{x}$ is obtained from any table of integrals as $\ln x$.* The last term of (2) is

$$20(\ln x_2 - \ln x_1) = 20 \ln \left(\frac{x_2}{x_1}\right) = 20 \ln \left(\frac{500}{200}\right) = 18.33 \text{ hr.}$$

Although the former approximate results are not greatly in error, the method of using average rates is to be avoided, as the errors introduced are usually impossible to estimate without carrying out the correct integration for comparison.

* $\ln x$ will be used to denote the logarithm of x to the base e and $\log x$ the logarithm of x to the base 10; $\ln x = 2.30 \log x$.

In passing, it may be noted that if the velocity of the car were linear in time the use of an arithmetic mean rate would be strictly correct. For example, if $V = 20\theta$, where V represents miles per hour and θ hours, calculate the distance covered between $\theta = 1$ and $\theta = 3$. The differential equation is

$$dx = V\,d\theta = 20\theta\,d\theta$$

and

$$x_2 - x_1 = 20\int_{\theta=1}^{\theta=3} \theta\,d\theta = \tfrac{20}{2}(9 - 1) = 80 \text{ miles}$$

At one hour the velocity is 20 m.p.h., and at three hours the velocity is 60 m.p.h. The arithmetic mean is 40 m.p.h., which corresponds exactly to 80 miles covered in 2 hr. This comparison emphasizes the point that the use of arithmetic mean rates may or may not be correct and should be employed with the utmost caution.

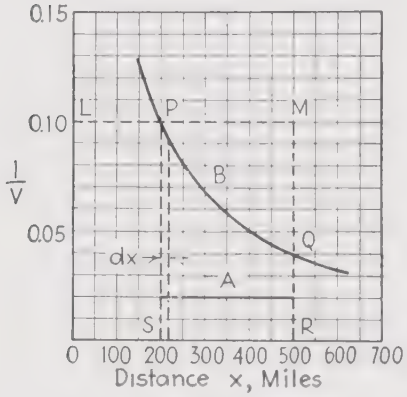


FIG. 2.—Graphical integration.

3. Graphical Integration. It may be noted in the preceding example that the time for each mile is the distance divided by the velocity prevailing for that mile. This may be expressed as dx/V, which may also be said to be the product of $1/V$ times dx. Values of $1/V$ for the two cases discussed above are plotted vs. the distance x in Fig. 2. The horizontal line A represents the case of constant velocity and curve B the case for which $V = 0.05x$. The product $(1/V)dx$ is represented by the product of the ordinate times the differential length dx. In the case of curve A, this is seen to be the area of a small rectangle having a width dx and a height 0.02. The total time is represented by the sum of such areas, which is the area of the rectangle of height 0.02 and width $x_2 - x_1$, or 300. If this area is expressed in terms of the units of $1/V$ and of x, the result is 300×0.02, or 6 hr.

In case B, the small rectangle becomes a narrow trapezoid, the top of which is not horizontal. If dx is made small enough, the height may be taken as constant and equal to $1/V$. The area of the figure $PQRS$ is then the summation of an infinite number of products of $(1/V)dx$. This summation is the process of integration, and it follows that

$$\text{Area } PQRS = \int_{x_1}^{x_2} \frac{dx}{V} = 20 \int_{x_1}^{x_2} \frac{dx}{x} = 18.33 \text{ hr.}$$

The integral may be used to obtain the area, or, conversely, the measurement of the area of such a plot may be used as a practical means of determining the numerical value of the integral between the limits x_1 and x_2, *i.e.*, the value of the definite integral.

The graphical evaluation of definite integrals is of great utility in the many cases where the algebraic form of the integral is difficult to evaluate or impossible to obtain. The procedure is fairly evident from the example cited above. In general, the problem is to evaluate an integral of the form $\int_{x_1}^{x_2} f(x)dx$, where $f(x)$ is a function of x [in case B, $f(x) = 1/V$]. The procedure is to plot $f(x)$ vs. x and measure the area under the curve, between the vertical lines at $x = x_1$ and $x = x_2$.

The area is most conveniently obtained by the use of a planimeter, although it may also be obtained by counting squares and fractions of squares if good cross-sectional paper is used. The result is obtained either as a planimeter reading or as a number of squares. It is important to be able to convert these values to the correct numerical value of the desired integral. The planimeter should be used not only to trace the figure to be measured but also to trace any convenient square or rectangle of approximately the same area. The lengths of the two sides of the rectangle (not in inches or centimeters but in units of the scales employed for ordinate and abscissa) are multiplied to obtain the area of the rectangle in the proper units. The desired integral is then obtained as the area of the rectangle multiplied by the ratio of the two planimeter readings.

Figure 2 may be employed to obtain the integral for case B by counting squares. Inspection shows the area of the figure $PQRS$ to be approximately 36.4 squares. The square $LMRO$ contains 100 squares and has an area of $0.10 \times 500 = 50$ (hr.). The value of the integral is, therefore, $\frac{36.4}{100} \times 50 = 18.2$ hr. This may be compared with the correct value of 18.33 hr.

As a further illustration of the method of plotting to be employed, consider the problem of evaluating the quantity of oil flowing in a round pipe, under conditions such that the flow is

viscous, and the velocity distribution across any pipe diameter is given by an expression of the form $V = f(r)$.

The radius of the pipe is R, V is the velocity at the distance r from the center line. In the face of the pipe cross section, consider any semicircular ring of width dr and length πr (see Fig. 3). The area of this differential ring is $\pi r\,dr$, and the flow through this element is $V\pi r\,dr$ cu. ft. per sec. The total flow for one-half the cross section of the pipe is the summation, or integration, of the flows through all such elements having radii between 0 and R. Since the flow in both halves of the pipe is the same, the total flow Q is given by

$$Q = 2\pi\int_0^R Vr\,dr \tag{3}$$

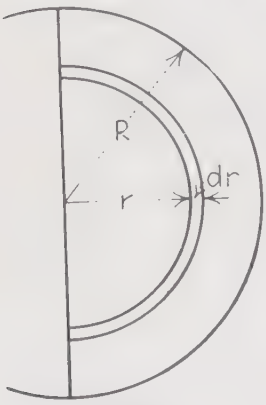


FIG. 3.

When the known relation between V and r is substituted,

$$Q = 2\pi\int_0^R f(r)r\,dr \tag{4}$$

This may or may not be integrable in the ordinary way, depending on the complexity of the function $f(r)$. It may be integrated quite easily by the graphical procedure, however. When the method described is followed, a plot is prepared of $rf(r)$ vs. r and the area under the curve between the limits 0 and R multiplied by 2π to give Q.

Since $r\,dr = \frac{1}{2}d(r^2)$, (4) may be written

$$Q = \pi\int_0^{R^2} f(r)d(r^2) \tag{5}$$

The integration may be performed graphically by preparing a plot of $f(r)$ vs. r^2 and measuring the area between $r^2 = 0$ and $r^2 = R^2$.

4. Graphical Construction of Integral Curves. The function $y = f(x)$ has associated with it an integral function $F(x)$ such that

$$\frac{dF(x)}{dx} = f(x) \tag{6}$$

and

$$F(x) = \int f(x)dx + C \tag{7}$$

The definite integral $\int_{x=a}^{x=b} f(x)dx$ has already been interpreted as the area bounded by the ordinates at $x = a$ and $x = b$ under the curve of $f(x)$ vs. x, and we now seek a graphical interpretation of the integral function $F(x)$. An obvious method of plotting $F(x)$ is to write first a definite integral with variable upper limit

$$F(x) = \int_{x=x_0}^{x=x} f(x)dx \tag{8}$$

By measuring the area under the curve $f(x)$ vs. x between the fixed ordinate at $x = x_0$ and the variable ordinate at $x = x$ and

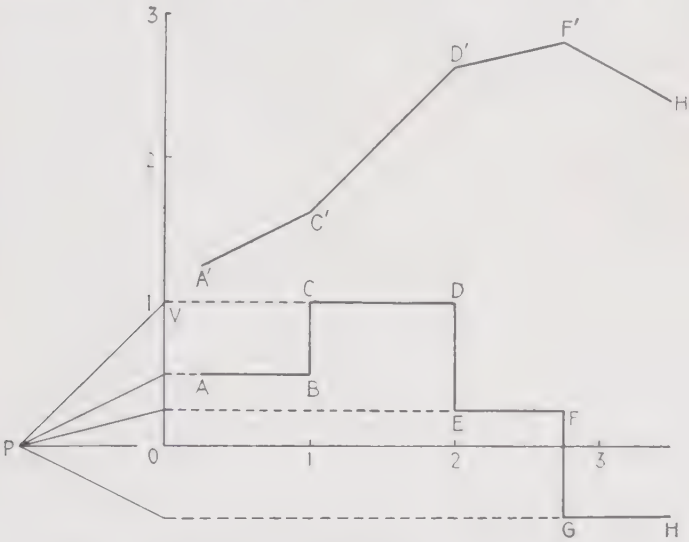


FIG. 4.—Construction of integral curve from step curve.

plotting this area against x, we may determine a curve for $F(x)$. The arbitrary selection of an initial point (x_0,y_0) on the integral curve is equivalent to assigning a definite value to the arbitrary constant C in (7). The integral function $F(x)$ is a function of an arbitrary constant C and therefore represents a family of curves, one of which may be plotted when a value is assigned to C.

The measurement of areas is frequently inconvenient and in any event unnecessary to the development of an accurate integral curve, in view of the relation expressed by (6). To illustrate the method, suppose that $f(x)$ is the stepwise curve $ABCDEFGH$ of Fig. 4. The initial point A' on the integral curve is selected at any convenient distance above A, and, since $f(x)$ has a constant value of 0.5 over the interval AB, by (6) $F(x)$ must proceed to C'

with a constant slope of 0.5. Similarly $C'D'$, $D'F'$, and $F'H'$ have slopes of 1.0, 0.25, and -0.5, respectively.

A convenient method of construction for determining the slopes is to lay off a distance OP to the left of the origin equal to one unit on the x axis. If the ordinate of a point C on the curve to be integrated is projected onto the y axis at V, the slope of the line PV is the same as the slope of the integral curve corresponding to point C, and $C'D'$ is parallel to PV. In many cases, the range of variation of x and y may be such that it would be impractical to use the same scale on the x and y axes. Under these circumstances, a simple relation may be derived between the length of the units on the x and y axes, the distance OP (called "the polar distance"), and the length of the unit that must be used to measure the ordinates of the integral curve. Let u_x and u_y be the lengths in terms of any unit (inches, centimeters or millimeters) on the x and y axes, respectively; p and u_i will be taken as the lengths of the polar distance OP and the length of the unit used to measure integral curve ordinates. Consider $f(x)$ over the interval CD. If the preceding construction is to be used and $C'D'$ taken parallel to PV, we must have

$$\frac{dF(x)}{dx}\frac{u_i}{u_x} = \frac{f(x)u_y}{p} \tag{9}$$

Since $[dF(x)/dx] = f(x)$, irrespective of the lengths of the various scales, (9) reduces to

$$u_i = \frac{u_y \cdot u_x}{p} \tag{10}$$

This is a necessary relation connecting the length of the polar distance p with the lengths of the units on the x and y axes and the length of the unit used to measure ordinates of the integral curve. In Fig. 4, $u_x = u_y = p = u_i$.

The procedure whereby this method of plotting integral curves may be extended to any function is illustrated in Fig. 5. With point A as a starting point a series of triangles is constructed about the curve to be integrated by means of a step curve. The step curve is constructed so that the areas of successive triangles below and above the curve are equal. The polar distance may now be laid off and the step curve integrated as in Fig. 4. The accuracy of the integral curve so obtained will depend upon how

many triangles are used and how closely the condition of equality of areas is approached. This method can be quite accurate in practice. The series of straight lines resulting from the construction may be smoothed into a curve when it is seen that at the abscissas B, C, D, and E the integral curve must be tangent to the straight lines. In Fig. 5, for purposes of illustration, if the length of the unit on the x axis is considered as 1, the length of the unit on the y axis will be 2 and the polar distance will be 2.5. Hence, by (10), the length of the unit used to measure ordinates of the integral curve must be $u_1 = (2)(1)\ 2.5 = 0.8$ times as long as the length of the unit on the x axis.

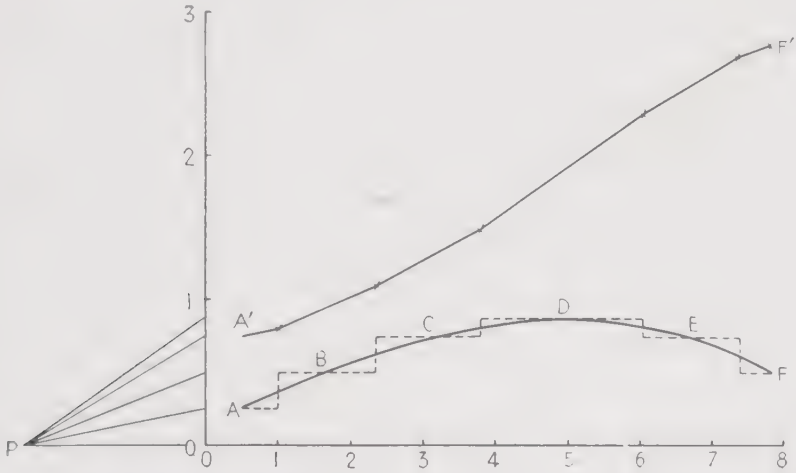


FIG. 5.—Construction of integral curve from step curve approximating a function.

5. Differentiation. As pointed out in the introduction, the fundamental natural laws on which engineering is based are frequently expressed in the form of differential equations giving the rate of change of an important quantity with respect to an independent variable. Particularly in the interpretation of experimental data, therefore, it is necessary to be able to carry out the process of differentiation, analytically, graphically, or numerically.

A function $y = f(x)$ expresses the relation between y and x. The rate of change of y with change in x, or the ratio of a differential change in y to the corresponding differential change in x, is called the "derivative" of the function. It is expressed as dy/dx, or $f'(x)$. The derivative, in turn a function of the independent variable x, is obtained by differentiating the function

with respect to x. The differential dy is the product of the derivative of the function times a differential increment in x. For example, in the simple case $y = ax^2$, the differential of y is $dy = 2ax\,dx$, and the derivative of the function is $2ax$. Not all functions have derivatives, since for such to exist it is necessary that the ratio of the increment of y, Δy to the increment of x, Δx approach a definite limit as Δx approaches zero. This limit is defined as the "derivative." In Fig. 6, for example, curve OBC represents a continuous function having no derivative at point B. The derivative, or "derived function," is plotted as shown by $OPQR$ and is seen to be discontinuous at B. Since the derivative has no *definite* value at B, the function has no derivative at B.

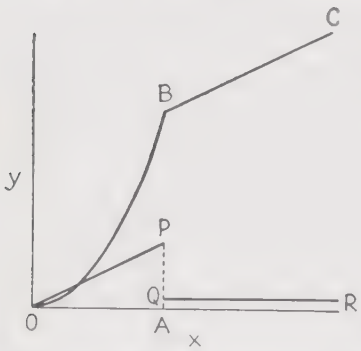


Fig. 6. Graph of function and derived curve.

From the definition of the derivative as dy/dx, it is clear that it is equal to the slope of a curve of y plotted vs. x. Thus in Fig. 6, the curve $OPQR$ is a graph of the slope of the line OBC. This relation suggests certain graphical and numerical methods of differentiation described below.

If the derived function $f'(x)$ is in turn differentiated, the second derivative $f''(x)$ is obtained. This may be written $\frac{d}{dx}\left(\frac{dy}{dx}\right)$, or d^2y/dx^2. The second derivative could be represented by a third curve on Fig. 6 and would be a plot of the slope of the curve $OPQR$. The second derivative is thus the rate of change with x of the rate of change of y with x. In the particular case referred to, there exists neither first nor second derivative at the point B. If the function relates distance to time, the first derivative is the velocity, and the second derivative represents acceleration. The third derivative d^3y/dx^3, or $f'''(x)$, is the derivative of $f''(x)$, etc.

In some of the problems to be discussed in later sections, it will be important to be able to interchange variables in derivatives. If y is replaced by z, where y is some function $f(z)$ of z, then by the ordinary rules of differentiation

$$\frac{dy}{dx} = f'(z)\frac{dz}{dx} \tag{11}$$

and

$$\frac{d^2y}{dx^2} = f''(z)\left(\frac{dz}{dx}\right)^2 + f'(z)\frac{d^2z}{dx^2} \tag{12}$$

If the independent variable x is to be replaced by another variable p, where $x = f(p)$, then

$$\frac{dy}{dx} = \frac{\dfrac{dy}{dp}}{\dfrac{dx}{dp}} = \frac{1}{f'(p)}\frac{dy}{dp} \tag{13}$$

and

$$\frac{d^2y}{dx^2} = \frac{d}{dx}\left(\frac{\dfrac{dy}{dp}}{\dfrac{dx}{dp}}\right) = \frac{f'(p)\dfrac{d^2y}{dp^2} - f''(p)\dfrac{dy}{dp}}{[f'(p)]^3} \tag{14}$$

If x and y are simply to be interchanged, we may substitute $p = y$ and (13) and (14) reduce to

$$\frac{dy}{dx} = \frac{1}{f'(p)} = \frac{1}{\dfrac{dx}{dy}} \tag{15}$$

and

$$\frac{d^2y}{dx^2} = -\frac{\dfrac{d^2x}{dy^2}}{\left(\dfrac{dx}{dy}\right)^3} \tag{16}$$

6. Graphical Differentiation. Since the derivative of a function at a particular value of x is the slope of the curve of y vs. x at that value of x, it follows that any means for measuring the slope of a curve may be employed to obtain the derivative.

One rather obvious method is to plot the function and obtain the slope with the aid of a straightedge. The latter is swung about the point on the curve until it is judged by eye best to represent the slope of the curve at the point, a straight line drawn for record, and the slope of the straight line calculated. In this last step, it is important to obtain the slope in terms of the variables, taking into account the scales used in ordinate and abscissa. Only where these are equal is the geometric slope the correct value.

A better way is to place a protractor or triangle on a fixed straightedge or tee square at a definite angle to the x axis and slide it along until it touches the curve representing the function. This procedure locates the point on the curve where the slope is equal to the predetermined value. As an aid in locating the exact point of tangency, several chords such as AB of Fig. 7 may be drawn parallel to the tangent. These are bisected, and a line QP is drawn through their mid-points to intersect the curve at the desired point P. Although the principle is quite similar to the direct measurement of the slope at a point, the results obtained are found to be somewhat better. With a graph of reasonable size, it is usually possible to obtain the derivative in this way with an error of about 3 per cent, although the accuracy varies considerably with the curvature of the line representing the function.

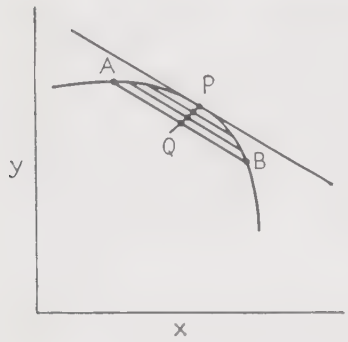


FIG. 7.—Graphical differentiation.

A very convenient device for measuring slopes of curves is a movable protractor fitted with a prism at the center. This is placed over the curve at the point in question and turned until the two branches of the curve seen through the two faces of the prism appear to join to form a smooth continuous curve. The slope of the curve with reference to the base of the instrument is read directly. Some of the instruments of this type on the market employ a protractor of such small diameter that the accuracy obtainable is no better than, if as good as, by the preceding methods.

7. Numerical Differentiation. Because of the necessity of being able to differentiate experimental data, it is important to have means of obtaining the derivative when an algebraic expression for the function is not given. Where this must be done more accurately than is possible by the graphical means described, resort is had to numerical processes, of which several are available. The general procedure is to represent the function in the region where the derivative is desired by an interpolation formula or some other empirical formula. When such a formula is obtained, the differentiation is quite easy, because the formulas employed for this purpose are usually of a fairly simple form

Interpolation formulas and curve fitting are discussed in Chap. VII.

8. Partial Differentiation. The engineer is fortunate if the relation with which he is dealing involves only two variables, being of the type $u = f(x)$. In the more general case, the variable u is dependent on two or more independent variables, and the function is of the form $u = f(x,y,z \cdots)$.

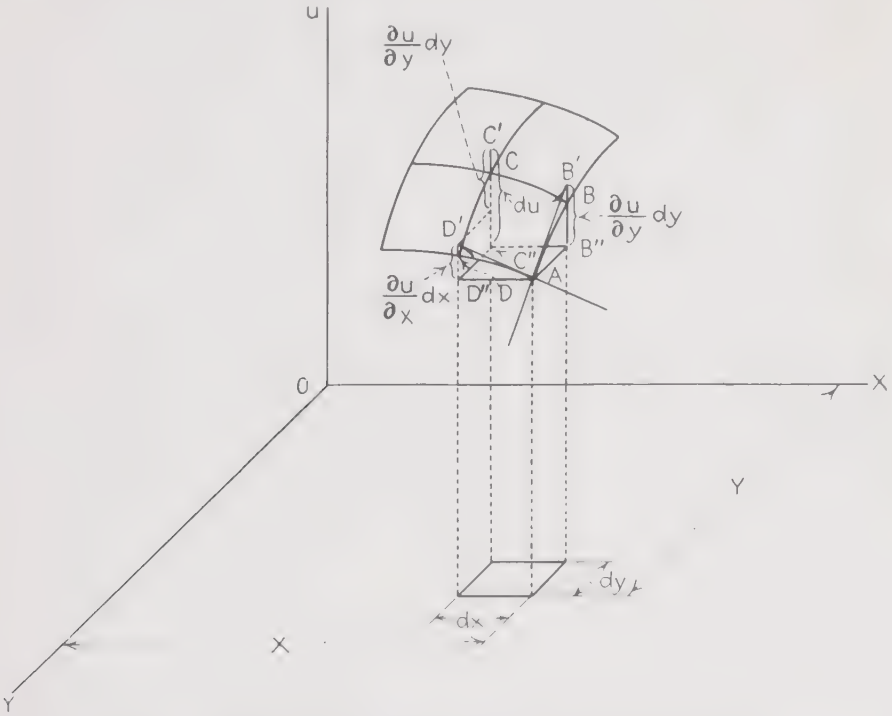


FIG. 8.—Geometrical representation of partial differentiation.

When there are but two independent variables, it is possible to represent the functional relationship geometrically on a three-dimensional diagram, as indicated by Fig. 8. The vertical height of a point such as A on a curved surface represents the value of the function at any given values of x and y. AB and DC represent lines drawn on this surface, parallel to the plane UOY, *i.e.*, for constant values of x. AD and BC are parallel to UOX and represent the variation in the function for constant values of y. If y changes by Δy, x remaining constant, the point representing the function moves to B and the increment in the function, represented by the line $B''B$, is written Δu_x. As in the case of two variables, this increment may be approximated by the

product of the slope of the curve AB at A and the increment Δy, (AB''). This slope is equal to the derivative of u with respect to y, taken under the assumption that x is constant, and is called the "partial derivative" of u with respect to y, its symbol being $\partial u/\partial y$. If Δy approaches zero as a limit, it becomes the infinitesimal increment dy and the product $(\partial u/\partial y)\cdot dy$ is, by definition, the partial differential of u at constant x. Since $\partial u/\partial y$ is the slope of tangent AB', the partial differential is represented by line $B''B'$ and is seen to differ from the increment by the line BB'. As dy approaches zero, BB' approaches zero and the differential becomes an increasingly better approximation to the increment. Similarly, if x changes by Δx, y remaining constant, the point representing the function moves to D and the increment in the function, represented by $D''D$, is written Δu_y. This increment is approximated by $(\partial u/\partial x)\cdot\Delta x$, $\partial u/\partial x$ being the derivative of u with respect to x taken under the assumption that y is constant, as it is along curve AD. The partial differential of u at constant y is then defined as $(\partial u/\partial x)\cdot dx$ (line $D''D'$). The total change in u, Δu, resulting from the increments Δx and Δy, is represented by line $C''C$ and is very closely approximated by the sum of the quantities $(\partial u/\partial x)\cdot\Delta x$ and $(\partial u/\partial y)\cdot\Delta y$. When Δx and Δy become the infinitesimal increments dx and dy, the change in u is an infinitesimal quantity defined as the total differential of u, du. The total differential is then given by

$$du = \frac{\partial u}{\partial x}\cdot dx + \frac{\partial u}{\partial y}\cdot dy \tag{17}$$

and is represented by line $C''C'$. This may also be expressed by saying that the total differential change in u is the rate of change of u with x times the differential change in x plus the rate of change of u with y times the differential change in y.

The first partial derivative of u with respect to x is a function of x and y and may itself be differentiated with respect to x, y being considered constant. This operation results in the second partial derivative of u with respect to x, written $\partial^2 u/\partial x^2$. If $\partial u/\partial x$ is differentiated with respect to y, x being held constant, the resulting second partial derivative is written $\partial^2 u/\partial x\cdot\partial y$. Similarly, differentiation of $\partial u/\partial y$ will yield the two second derivatives $\partial^2 u/\partial y^2$ and $\partial^2 u/\partial y\cdot\partial x$. It can be shown that

$\partial^2 u / \partial x \cdot \partial y = \partial^2 u / \partial y \cdot \partial x$ and, in general, the value of higher mixed partial derivatives is independent of the order of differentiation.

As a simple example of partial differentiation, we may take the gas law

$$T = \frac{pv}{R} \tag{18}$$

If we construct a rectangle (Fig. 9) such that the width is equal to p and the length equal to v, the area A divided by R must equal T. If p and v undergo the differential changes dp and dv, the differential of T is, by (17)

$$\begin{aligned} dT &= \frac{\partial T}{\partial p}dp + \frac{\partial T}{\partial v}dv \\ &= \frac{v}{R}dp + \frac{p}{R}dv \end{aligned} \tag{19}$$

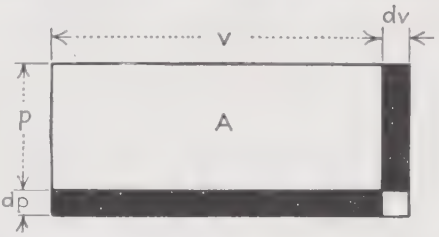


FIG. 9.

This result could also have been obtained by applying the rules for differentiation of the product of two quantities. The increment in T resulting from increments dp and dv is proportional to the total increase in area of the rectangle, *i.e.*, the sum of the shaded rectangles and the small corner square. The differential of T is seen to be proportional to the sum of the shaded areas

$$v\,dp + p\,dv$$

and differs from the true increment by a small area proportional to the product of the differentials $dp \cdot dv$. This small area $dp \cdot dv$, being an infinitesimal of higher order than either dp or dv, is negligible.

9. Maxima and Minima. Since the derivative dy/dx, or $f'(x)$, represents the rate of change of y with change in x, it is evident that if the function passes through a maximum or minimum the derivative will be zero. If the occurrence of such a maximum or minimum is to be determined and located, the derivative is equated to zero, thus giving the condition for which the maximum or minimum exists. This procedure is of considerable value in engineering calculations, since the location of a maximum or minimum is frequently of great practical importance. This is particularly true in chemical-engineering plant design, since the optimum operating and design variables are to be determined in order that the maximum profit will result.

In Fig. 10, the curve $ABCDE$ represents the function $y = f(x)$. The values of y in the neighborhood of points A and C are all less than the value of y at A and C, and the function is said to go through a maximum at these points. Similarly, because the values of y in the neighborhood of B are all greater than the value of B, the function is said to go through a minimum at B. This curve emphasizes that the terms "maximum" and "minimum" do not necessarily denote the greatest and the least possible values a function may assume.

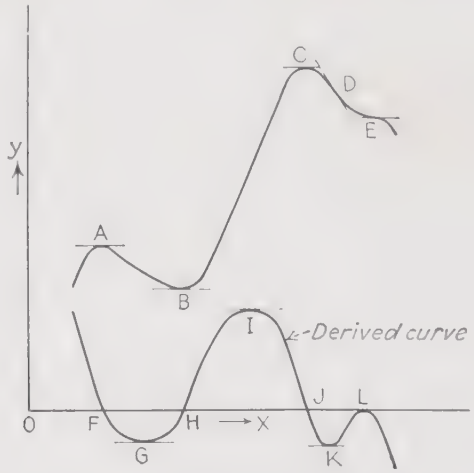


FIG. 10.—Function having maxima and minima and derived curve.

It is evident geometrically that the slope of the curve is zero at the maximum and minimum points, and since the slope is given by the derivative dy/dx, or $f'(x)$, these points may be determined and located by solution of the equation $f'(x) = 0$. The roots of this equation merely locate the maximum and minimum points and cannot distinguish between them. Furthermore, the condition locates such points as E. One method of distinguishing among points A, C, and E is to calculate values of $f(x)$ in their immediate vicinity. An alternative method, often more convenient, is to evaluate the second derivative at these points. In Fig. 10, curve $FGHIJKL$ is a graph of dy/dx vs. x. The slope of this curve is d^2y/dx^2, or $f''(x)$. This slope is negative at those values of x for which $f(x)$ has a maximum and positive at those values of x for which $f(x)$ has a minimum. The second derivative is zero at point E. The slope of the derived curve is zero at those points on $y = f(x)$ where the tangent crosses the curve.

These are known as "points of inflection." A convenient table of these relations follows:

Maximum	Minimum
$dy/dx = 0$	$dy/dx = 0$
$d^2y/dx^2 < 0$	$d^2y/dx^2 > 0$

If the function does not pass through either a maximum or minimum, this will be indicated in some way by the expressed condition, as by giving the square root of a negative number when solved for the dependent variable.

Calculations to determine the optimum conditions from the point of view of costs and monetary return are termed "economic balances." The basic criterion of the true optimum is maximum return on the investment, but the problem frequently simplifies to one of determining the minimum cost, the maximum production from a given piece of equipment, the minimum power, etc. The quantity considered is expressed as a function of the design or operating variables. On differentiating and equating to zero, we find the condition which determines the optimum value of the variable under control.

As an example, consider the two-stage reversible adiabatic compression of a gas from an initial pressure p_1 to a final pressure p_3. If the fixed charges on the compressors are assumed to be essentially independent of the interstage pressure employed, then the optimum operation involves the determination of the interstage pressure for which the total power requirement is a minimum. For a fixed gas flow, this corresponds to the minimum work for the two stages. If the gas enters at T_1 and is cooled to T_1 between stages, the total work is given by

$$W = NRT_1 \frac{k}{k-1}\left[\left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}} - 2 + \left(\frac{p_3}{p_2}\right)^{\frac{k-1}{k}}\right] \qquad (20)$$

where N represents the lb. mols of gas compressed, R is the gas constant (1,544), k is the ratio of specific heat at constant pressure to specific heat at constant volume for the gas compressed, and T_1 is the inlet gas temperature, °F. abs.; W then represents the total work as ft.-lb. If this quantity is to be a minimum, then the derivative must be zero.

$$\frac{dW}{dp_2} = NRT_1\frac{k}{k-1}\left[\left(\frac{k-1}{k}\right)p_1^{\frac{1-k}{k}}p_2^{-\frac{1}{k}} - \left(\frac{k-1}{k}\right)p_3^{\frac{k-1}{k}}p_2^{\frac{1-2k}{k}}\right] = 0$$

Solving for the value of p_2 that satisfies this condition, we find

$$p_2^{\frac{2k-2}{k}} = p_3^{\frac{k-1}{k}}p_1^{\frac{k-1}{k}}$$

or

$$p_2 = \sqrt{p_1 p_3} \tag{21}$$

This is the relation found in handbooks for the optimum interstage pressure in a two-stage compression. Since k does not enter into the result, it is apparent that the equation will hold for any polytropic compression in which it is allowable to replace k by a constant exponent n.

In plant-design problems, it is common to require the optimum operating variable for the optimum design. For example, a surface condenser receiving the exhaust steam from a turbine may be either large or small, and for each size the water rate may vary widely. For a condenser of a fixed size, the steam costs will be large if the water rate is low; for the exhaust pressure will be high owing to a large increase in cooling-water temperature. If high water rates are used, the temperature rise of the cooling water will be small, the condenser pressure low, and the steam costs low, but the water cost will be great. A balance must be struck between steam and water costs to determine the optimum water rate. This process must be repeated for each condenser size until the minimum total of water costs, steam costs, and fixed charges on the condenser is obtained. In general, the total costs u may be expressed in terms of the water rate x and the condenser size y, *i.e.*,

$$u = f(x,y)$$

Evidently the economic problem of determining minimum total cost reduces to the mathematical problem of determining the minimum value of a function of two independent variables. If $f(x,y)$ is to have a minimum at x_1, y_1, it is clear that the functions $f(x,y_1)$ and $f(x_1,y)$, in which one variable appears, must have

a minimum at this same point. This means that at x_1, y_1 it is necessary for $\partial u / \partial x$ and $\partial u / \partial y$ to equal zero and we may determine x_1, y_1 as the values of x and y satisfying the two simultaneous equations

$$\frac{\partial u}{\partial x} = 0, \qquad \text{and} \qquad \frac{\partial u}{\partial y} = 0$$

If four variables are involved, three conditions must be met to determine the optimum values of three independent variables, etc.

The compressor problem quoted above may be extended to a three-stage compression, and optimum values of two interstage pressures obtained. The results are $p_2 = \sqrt[3]{p_1^2 p_4}$ and $p_3 = \sqrt[3]{p_4^2 p_1}$.

As another example, consider the extraction of acetic acid from a dilute solution in water by means of a quantity of benzene. The total benzene B will be divided into three quantities b_1, b_2, and b_3 for use in three separate extractions of the aqueous layer. The acetic acid concentration in the original a volumes of aqueous layer is x_0. Assume no volume change on mixing, and the distribution law to hold with equilibrium between phases after each extraction, *i.e.*, $y_1 = Kx_1$, $y_2 = Kx_2$, and $y_3 = Kx_3$, where the subscripts refer to the number of the extraction. By a material balance for the first extraction,

$$ax_0 = b_1 y_1 + ax_1 = b_1 K x_1 + ax_1$$

Hence,

$$x_1 = \frac{ax_0}{a + b_1 K}$$

Similarly,

$$x_2 = \frac{ax_1}{a + b_2 K}$$

and

$$x_3 = \frac{ax_2}{a + b_3 K} = \frac{a^3 x_0}{(a + b_1 K)(a + b_2 K)(a + b_3 K)} \tag{22}$$

To obtain the most complete extraction with the allowed quantity B of benzene, x_3 should be a minimum. Since $a^3 x_0$ is fixed, the denominator of (22) should be a maximum. Represent the denominator by u, and equate the partial derivatives with respect to b_1 and b_2 to zero (note that $B = b_1 + b_2 + b_3$).

$$u = (a + b_1K)(a + b_2K)(a + b_3K)$$
$$= (a + b_1K)(a + b_2K)(a + BK - b_1K - b_2K)$$

$$\frac{\partial u}{\partial b_1} = (a + b_2K)[(a + BK - b_1K - b_2K)K - (a + b_1K)K] = 0$$

$$\frac{\partial u}{\partial b_2} = (a + b_1K)[(a + BK - b_1K - b_2K)K - (a + b_2K)K] = 0$$

from which

$$B - b_1 - b_2 = b_3 = b_1$$

and

$$B - b_1 - b_2 = b_3 = b_2$$

i.e.,

$$b_1 = b_2 = b_3$$

In this particular case, the result may have been foreseen from the symmetry of the operations, but the example serves to illustrate the procedure. It is perhaps obvious that the result is general and that equal portions of solvent should be used for maximum extraction, no matter how many divisions are made of the solvent B.

The location of a maximum or minimum becomes obvious if the function is plotted, and this alternative procedure may be followed in economic balance calculations. The analytical method has the advantage of directness and simplicity in many cases. The graphical method involves calculation of the function at a number of points, and usually requires considerably more time to obtain the result. When the curve is obtained, however, its shape indicates the importance of operating at the exact optimum. If the curve is flat, a considerable variation in operating conditions will not affect the costs or profits appreciably. If the maximum or minimum is sharp, it may be quite important to operate at the optimum point. If the calculation of costs contains a graphical step, such as the use of a humidity chart, it may not be possible to obtain an analytical function for differentiation. An empirical equation may be substituted for the plot used in the graphical step and the analytical method followed if the resulting cost function is not too complicated. The graphical procedure of plotting the function may be followed in any case.

10. Evaluation of Indeterminate Fractions. L'Hôpital's Rule. Not infrequently, the fraction $f_1(x)/f_2(x)$ will give rise to one of

the indeterminate forms $0/0$ or ∞/∞ at some particular value of x, $x = a$. In such a case, the value of the function at $x = a$ is defined as the limit of the value approached by the function as x approaches a.

$$\frac{f_1(a)}{f_2(a)} = \lim_{x \to a} \frac{f_1(x)}{f_2(x)} \tag{23}$$

This limit may sometimes become evident upon algebraic rearrangement. Consider the fraction $(x - a)/(x^2 - a^2)$, which reduces to $1/(x + a)$ after division of numerator and denominator by $x - a$. When $x = a$, the fraction becomes $0/0$. The value at $x = a$ is obtained from definition (23) as $1/2a$ because as $x \to a$

$$\lim_{x \to a} \frac{x - a}{x^2 - a^2} = \lim_{x \to a} \frac{1}{x + a} = \frac{1}{2a}$$

A more general procedure for the evaluation of such fractions is indicated by L'Hôpital's rule, which is derived in most texts on calculus. When the rule is followed, both numerator and denominator are differentiated with respect to x and the desired value of the original fraction obtained as the ratio of the derivatives, evaluated at $x = a$

Expressed mathematically,

$$\lim_{x \to a} \frac{f_1(x)}{f_2(x)} = \frac{f_1'(a)}{f_2'(a)}, \qquad \text{when} \qquad \frac{f_1(x)}{f_2(x)} = \frac{0}{0} \text{ or } \frac{\infty}{\infty} \qquad \text{at} \qquad x = a$$

If the fraction obtained is again indeterminate, the rule may be applied again. Sometimes the process must be repeated two or three times before a finite value is obtained.

An equation encountered in absorption, distillation, extraction, and leaching is of the form

$$y = \frac{x^{n+1} - x}{x^{n+1} - 1} \tag{24}$$

In gas absorption, with systems where Henry's law applies to the gas-liquid equilibrium, y represents the fraction of solute in the inlet gas that is absorbed in a tower of n perfect plates, and x represents the ratio of solute-free liquor rate to gas rate, divided by the Henry's law constant. In practice, this equation is used rather widely, with x varying from zero to very large numbers. No trouble is experienced except when x is unity, resulting in the

fraction 0/0. On application of L'Hôpital's rule, the ratio of the derivative of the numerator to the derivative of the denominator becomes

$$\frac{(n+1)x^n - 1}{(n+1)x^n}$$

which reduces to $n/(n+1)$, the desired value of y for $x = 1$.

An expression giving rise to an indeterminate form such as $0 \cdot \infty$, $\infty - \infty$, 0^0, ∞^0, or 1^∞ may usually be rearranged to give a fraction taking the form 0/0 or ∞/∞ and evaluated by L'Hôpital's rule.

CHAPTER II

THE USE OF DIFFERENTIAL EQUATIONS

11. Problems Involved in Processes Occurring under Variable Conditions. The mathematical treatment of engineering processes involves three basic steps: the expression of the problem in mathematical language, the appropriate mathematical operations, and the interpretation of the results. The first frequently involves setting up a differential equation, and, although the procedure is not inherently complicated, it is with this first step that engineers often experience the greatest difficulty. No general procedure can be specified for the problem of setting up the differential equation, and it is believed that the best understanding of the methods is to be obtained by following a number of illustrative examples.

The practical value of a differential equation lies in the fact that it affords a connection between a simple basic physical or chemical law and a frequently complex relation of several variables of engineering importance in a practical problem. The application of even the simplest physical law to a process taking place under variable conditions may result in a relation of some complexity.

Consider, for example, a common type of flow process in which a precipitation is being carried out by mixing two streams A and B to form a third stream C in which the precipitate is carried away. Figure 11 represents the process diagrammatically. The reaction is extremely rapid, and agitation will be assumed to be so efficient that the material in the tank has substantially the same composition at all points. Streams A and B enter at the rate of a and b cu. ft. per min., respectively. Change in volume due to reaction may be neglected, so that stream C leaves at the rate of $(a + b)$ cu. ft. per min.

To ensure proper quality of the precipitate, it is necessary to maintain the acidity of the tank contents at n_0 lb. acid per cu. ft., with an allowable variation of $\pm p$ lb. per cu. ft. The acidity of the bath is maintained by a negligibly small volume of acid car-

ried by stream A. On the assumption that the acid supply fails suddenly at a time when the concentration is n_0, it is desired to develop the law relating acid concentration and time in order to estimate what time would elapse before this concentration falls below the allowable level. During this time, all other flows will be assumed constant.

It is apparent that under the conditions granted the only law of importance in this situation is the law of conservation of matter. This is expressed in the form of a so-called "material balance"

$$\text{Input} - \text{output} = \text{accumulation}^*$$

In the case of the problem outlined, a material balance on the

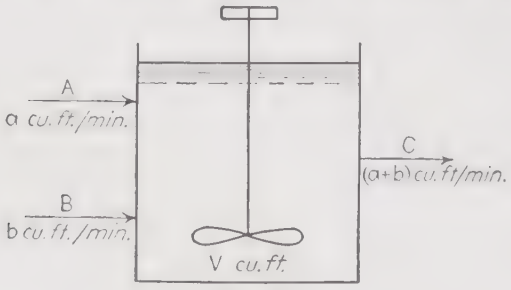


FIG. 11.

acid is significant, with input zero immediately upon failure of the acid supply.

In contrast to the simplicity of the basic material balance, it may be shown that the relation between the critical time θ_c and the concentration $(n_0 - p)$ is given by the formula

$$\theta_c = 2.3\left(\frac{V}{a+b}\right)\log_{10}\left(\frac{n_0}{n_0 - p}\right) \tag{1}$$

where V is the volume of liquid in the tank. In order to obtain this relation, the basic material balance is expressed in the form of a differential equation and integration performed between appropriate limits. The result is much more complicated than the basic law, because it relates variables in a process where conditions are changing continually.

12 Solution by Difference Equations and Summation of Finite Increments. It is possible to effect great simplification

* When output is greater than input, accumulation is negative and is often called "depletion"; accumulation = −depletion.

in the analysis of the problem just described by picturing what is happening over a very short interval of time during the process. The concentration of acid in the tank at any instant is n lb. per cu. ft., and the quantity of acid in the tank is Vn. Acid is flowing out of the tank at the rate of $n(a + b)$ lb. per min. Over a short period of time $\Delta\theta$, the acid concentration changes by Δn to become $(n + \Delta n)$, and the accumulation of acid in the tank is the difference between the amount present at θ and the amount present at $\theta + \Delta\theta$.

$$\text{Accumulation} = V(n + \Delta n) - Vn = V\Delta n$$

The output of acid over time interval $\Delta\theta$ is given by the product of average concentration over this time n_{av} and the volume of effluent, $(a + b)\Delta\theta$. By the material balance

$$\begin{aligned} &-\text{Output} = \text{accumulation} \\ &-n_{av}(a + b)\Delta\theta = V\,\Delta n \end{aligned} \tag{2}$$

Before an equation of this type becomes useful, it is necessary to determine the value of n_{av}. What type of average should be employed? Granting for purposes of illustration the applicability of an arithmetic average value of n at the beginning and end of the interval $\Delta\theta$, an obvious stepwise method of solution suggests itself. Starting with $n = n_0$, assume a small change in n, Δn, and calculate n_{av} as $(2n + \Delta n)/2$. Substitute this value of n_{av} into (2), and solve for $\Delta\theta$, obtaining the time θ at which $n = n + \Delta n = n_1$. Repeat this process, assigning an increment to n_1, Δn_1, and, upon substitution of a new value of

$$n_{av} = \frac{(2n_1 + n_1)}{2},$$

obtain a corresponding time increment. Repeat the process until enough increments of n have been taken to cause it to reach its critical value $(n_9 - p)$ at which time the sum of all the time increments will approximate θ_c.

13. Solution by Differential Equations or Summation of Infinitesimal Increments. Obviously, the greater the accuracy desired in θ_c, the smaller one must take the increments Δn so that the arithmetic mean value of n over an interval $\Delta\theta$ will more nearly equal the true value of n_{av}. The great disadvantage of this method of solution is the excessive labor required to obtain an answer that is at best only approximate.

Although there are many cases in chemical engineering where the relationship between the variables is so complex that this stepwise method becomes the only practical procedure, it is fortunate that in many cases such as the present problem an exact solution may be obtained by application of the calculus. Equation (2) may be rearranged to read

$$\frac{\Delta n}{\Delta \theta} = \frac{-n_{av}}{V}(a + b) \tag{3}$$

n is a function of θ, and as $\Delta\theta \to 0$, $\Delta n \to 0$. It will be recalled that by definition of the derivative

$$\lim_{\Delta\theta \to 0} \frac{\Delta n}{\Delta \theta} = \frac{dn}{d\theta} \tag{4}$$

Furthermore, as $\Delta\theta \to 0$, n_{av} approaches the value of n at time θ, and (3) may be written

$$\frac{dn}{d\theta} = -\frac{n}{V}(a + b) \tag{5}$$

Multiplying by $d\theta/n$ gives

$$\frac{dn}{n} = -\frac{(a + b)}{V} d\theta \tag{6}$$

Each side of (6) contains only one variable and may be integrated. The limits of the integrations are obtained if it is recalled that when $n = n_0$, $\theta = 0$, and when $n = n_0 - p$, $\theta = \theta_c$.

$$-\int_{n=n_0}^{n=n_0-p} \frac{dn}{n} = \int_{\theta=0}^{\theta=\theta_c} \left(\frac{a + b}{V}\right) d\theta \tag{7}$$

Integration gives

$$\ln \frac{n_0}{n_0 - p} = \left(\frac{a + b}{V}\right)\theta_c \tag{8}$$

Equation (1) is obtained by rearrangement of (8) and a change to decimal logarithms.

Equations of the type of (2), involving variables and finite increments of the variables, are known as "difference equations," and equations of the type of (4), involving variables and their infinitesimal increments or differentials, are known as "differential equations."

Though the utility of a differential equation has just been demonstrated by its power in analyzing a simple process occurring under variable conditions, a much deeper insight into its nature will be obtained by considering its mathematical origin (see Par. 16).

14. Functional Relationships. Whenever a relationship exists between two variables x and y such that for every value of x

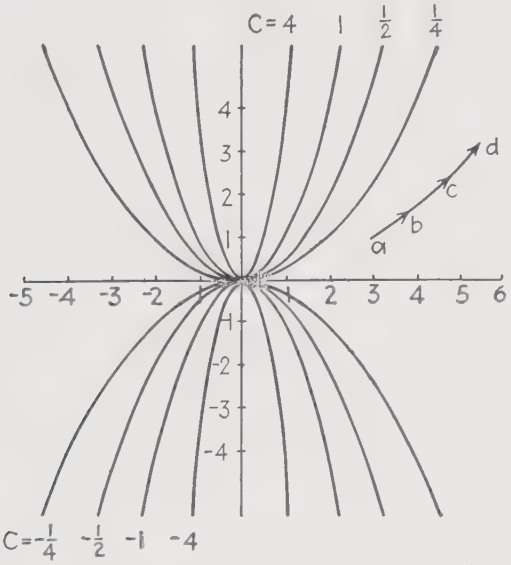


FIG. 12.—Family of parabolas with vertices at the origin.

there exists at least one value of y, y is said to be a function of x and the functional relation may be expressed symbolically as

$$f(x,y) = 0 \tag{9}$$

Equation (9) may be solved for either x or y, and it will be supposed that an arbitrary constant* c enters into the solution. Consider, for example, a parabola with vertex at the origin

$$f(x,y) = cx^2 - y = 0 \tag{10}$$

$$y = cx^2 \tag{11}$$

Equation (11) represents a family of parabolas with vertices at the origin as shown in Fig. 12, and in order to specify any particular parabola it is necessary to specify the value of c. This

* Arbitrary constants are constants to which any value may be assigned at pleasure, as opposed to absolute constants such as 1, 2, π, e.

fact may be indicated in the general Eq. (9) by the inclusion of c as follows:

$$f(x,y,c) = 0 \tag{12}$$

15. Use of Differential Equations in the Representation of Functions. Graphical Interpretation of Differential Equations. It is possible to represent this same family of curves by differentiating (11) and eliminating c.

$$\frac{dy}{dx} = 2cx \tag{13}$$

$$\frac{dy}{dx} = 2\frac{y}{x} \tag{14}$$

In (14), the arbitrary constant c has disappeared and in its place we are given the slope of a curve at any point in the x-y plane. Imagine starting at the point a at $x = 3$, $y = 1$, Fig. 12, and moving in the direction of the curve at this point where $dy/dx = \frac{2}{3}$. As soon as we leave the point a, the slope changes but we may, as a first approximation, consider the slope constant at $\frac{2}{3}$ until we have traveled a short distance ab. At b, we shall calculate a new slope as $2(y_b/x_b)$ and travel in a straight line in this direction to c, where we shall recalculate the slope as $2(y_c/x_c)$ and repeat the process. Obviously, the smaller the distances ab, bc, cd, etc., the more nearly it is possible to trace out the true curve passing through the point (3,1), *i.e.*, $y = \frac{1}{9}x^2$.

Following a similar procedure, it is possible to obtain a graphical interpretation of the stepwise method of solution proposed in the acid-dilution problem of Par. 11.* Assume a small increment in x, $\Delta x = dx_1$, and calculate dy from (14). The smaller the step Δx, the closer point b can be located on the true curve through a. By repeated selection of Δx's and the corresponding calculation of Δy's, the curve passing through point a can be traced approximately.

16. Mathematical Origin of Differential Equations and the Significance of Constants. It is important to recognize that

* It is of interest to note the similarity between the present discussion and the method of graphical integration described in Par. 4. The essential difference between the two cases is that in the case of evaluating a simple integral the slope of the integral function dy/dx is a function of x only, whereas in the more general problem proposed by a differential equation dy/dx is a function of both x and y.

before any curve could be traced using the differential Eq. (14) it was necessary to start at some definite point. This is equivalent to specification of a definite value for the arbitrary constant c in (11).

Equation (11) may be obtained from (14) by integration.

$$\int \frac{dy}{y} = 2\int \frac{dx}{x} \tag{15}$$

$$\ln y = 2 \ln x + c' \tag{16}$$

Placing $\ln c = c'$ gives

$$\ln y = \ln cx^2 \tag{17}$$

$$y = cx^2 \tag{11}$$

Notice that the arbitrary constant c that was eliminated when the differential equation was formed reappears upon solution by integration.

Equation (14) is said to be the differential equation of the family of curves represented by (11), and (11) is known as the primitive of the differential Eq. (14). If the primitive contains only one arbitrary constant, the differential equation will contain the variables and a first derivative. If the primitive contains two arbitrary constants, it is necessary to differentiate twice in order to eliminate the two constants and the differential equation will involve a second derivative.

For example, the differential equation of the family of parabolas with vertices on the x axis and axes parallel to the y axis is obtained as follows:

$$y = c(x - a)^2 \tag{18}$$

$$\frac{dy}{dx} = 2c(x - a) \tag{19}$$

$$\frac{d^2y}{dx^2} = 2c \tag{20}$$

Eliminating c and a from (18), (19), and (20) gives

$$2y\frac{d^2y}{dx^2} = \left(\frac{dy}{dx}\right)^2 \tag{21}$$

Similarly, since the equation representing the most general parabola in the x-y plane

$$ax^2 + by^2 + cxy + dx + ey + f = 0$$

contains six arbitrary constants, the differential equation representing *any* parabola in *any* position will involve a sixth derivative. Seven equations including the primitive and the six equations resulting from six successive differentiations will be required to eliminate the six constants. Under ordinary circumstances, it is not necessary to represent a parabola by such a complicated equation, since the coordinate axes may be located so that the equation assumes a simple form.

17. Definition of Terms. It is desirable at this point to introduce the definition of a few terms that are in common use in the discussion and classification of differential equations.

The order of a differential equation is the order of the highest derivative occurring in the equation.

The degree of a differential equation is the power to which the highest derivative is raised when the equation has been rationalized and cleared of fractions.

The differential equation

$$\frac{d^2y}{dx^2} = f(x)\left[1 + \left(\frac{dy}{dx}\right)^2\right]^{\frac{3}{2}} \tag{22}$$

represents the curvature of a liquid interface. It is of the second order and the second degree, as may be seen by applying the preceding rules after squaring both sides.

The solution of a differential equation involving the most general possible relationship among the variables is known as the "general solution" or the "primitive."

When the constants in the general solution are allowed to take on values corresponding to the conditions in a specific problem, the resulting equation is known as a "particular solution" of the differential equation because it is now applicable to but one particular case. $y = cx^2$ is the general solution of (14), and $y = \frac{1}{9}x^2$ is a particular solution.

The limitations introduced in obtaining a particular solution from a general solution are known collectively as the "boundary conditions" of the problem. Thus, c was determined as $\frac{1}{9}$ from the fact that out of the whole family represented by (11) the particular parabola of interest passed through the point (3,1).

Differential equations are divided into two general classes. Equations containing ordinary total derivatives or differentials are known as "ordinary differential equations," and equations

containing partial derivatives or differentials are known as "partial differential equations."

18. Physical Origin of Ordinary Differential Equations. Ordinary differential equations arise from those systems in which all the quantities may be taken as a function of a single independent variable. It is easy to test for the presence of a single independent variable from knowledge of the physical situation at hand.

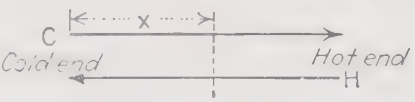


FIG. 13.

For example, in a single-pass countercurrent heat exchanger operating under fixed end conditions (Fig. 13) it is necessary only to specify the position in the exchanger by means of one variable, such as the distance x from the cold end, and all the other variables at this point are fixed by the physical laws controlling the system. In a continuously operated absorption tower (Fig. 14), liquid and gas compositions vary throughout the tower, but, if the end conditions are fixed, it suffices (if channeling effects are neglected and concentrations are assumed equal at all points across any cross section) to specify position in order to calculate the properties of both the liquid and gas streams.

FIG. 14.

In each of these cases, we may look upon either position or time of contact as the independent variable, since specification of x in the heat exchanger or h in the tower is equivalent to specification of the time of contact between two streams flowing by each other at known rates.

19. Physical Origin of Partial Differential Equations. Suppose now that the end conditions in the two preceding cases are not steady or constant with time. The rate of flow of the cold stream to the heat exchanger may vary with time, or the rate of flow of the solvent liquid to the tower may vary with time according to some known relation. In this case, we are dealing with unsteady-state conditions, and in order to specify conditions completely at any point in either apparatus we must specify the values of two independent variables: position, and either time or rate of flow of the variable stream. In this case, the instantaneous behavior of the system will be expressed by an equation involving the variables and their partial derivatives.

It is possible for partial differential equations to arise in the presence of steady operating conditions. Figure 15 illustrates a simple case of cross-flow heat exchange. This case differs from countercurrent or parallel-flow heat exchange in that the temperature of neither stream is constant across a cross section of the apparatus. The point at which either of the streams has reached

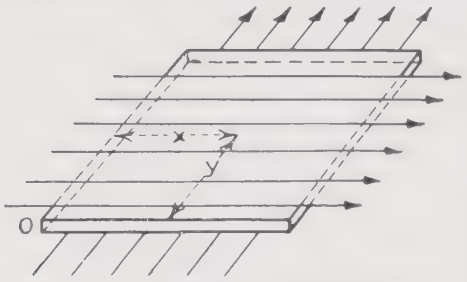


FIG. 15.—Cross-flow heat exchanger.

a specified temperature is located only by fixing the values of two position variables x and y. Another common example is shown in Fig. 16, which represents a portion of the cross section of a furnace wall. The interior and exterior surfaces of the furnace are maintained at t_h and t_c, respectively. The temperature within the furnace wall is a function of two independent position variables. During periods of heating and cooling the furnace, a third independent variable, is introduced, for the temperature of the interior of the furnace is not constant at t_h but varies with time.

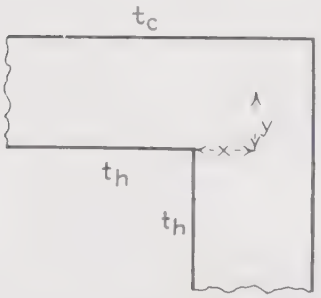


FIG. 16.—Corner junction of furnace walls.

20. Choice of Coordinate System. In some cases, it is possible to eliminate one variable by a proper choice of the coordinate system. As a simple example, we may suppose that it is desired to write an expression for the location of a moving point whose locus is a straight line going through the origin with a slope of unity. The desired expression is $y = x$. If the coordinates are tilted by 45 deg., the straight line coincides with the new x axis, and the value of x locates the point.

A differential equation in three variables, two of which are independent, is a partial differential equation. If a change of coordinates makes it possible to eliminate one variable, the

equation may be reduced to an ordinary differential equation and be much easier to solve. If the equation involves partial derivatives with more than three variables, the change of coordinates may simplify the equation sufficiently so that a solution may be obtained. The problem of heat conduction in a cylinder, treated in Chap. VI, is an example. Because the temperature may be seen to be symmetrical about the axis of the cylinder, a change to cylindrical coordinates makes it possible to simplify the partial differential equation by the elimination of one variable.

It is important to recognize that in those processes where there are two independent variables one may be held constant at any desired value with the obvious result that there are no partial derivatives. An ordinary differential equation may be used to describe the process for this one value of the second variable. Steady-state operating conditions in an apparatus are the physical equivalent of the mathematical condition that at any point in the apparatus the partial derivatives of all quantities with respect to time shall vanish.

21. Time As a Variable in Flow Processes. In processes involving the flow of material through an apparatus, confusion often arises because of the several statements that may be made with respect to time as a variable. This confusion is perhaps due to different uses of the terms "time" and "time of contact." When the absorption tower in Fig. 14 is operating under steady-state conditions, the liquid and gas streams L and G are flowing in at rates unchanging with time. A mass of gas entering the bottom of the tower has had a definite time of contact with the liquid stream by the time it reaches the cross section a distance h from the bottom. This time of contact between the two streams is a function of the distance h and the velocity of flow and is constant with respect to time as long as steady-state conditions are maintained. Furthermore, at any point in the tower, the values of all quantities are constant with time and the derivatives of all these quantities with respect to time are zero. These are really partial derivatives because they are taken at a constant value of h or, what really amounts to the same thing, the time of contact over the distance h. On the other hand, as we allow h to vary and move either up or down in the tower conditions change. For example, liquid concentration changes at a certain rate with change in h or time of contact, and the derivative of

liquid concentration with respect to time of contact has a finite value.

Marked changes occur if an unsteady-state condition is induced in the tower. This would occur if the rate of flow of gas stream G should start to vary with respect to time. In this case, conditions at any cross section h will change with respect to time, and it is proper to speak of the rate of change of time of contact with time at a given value of h, this rate of change being a partial derivative. Similarly, the rates of change of the other dependent variables with time at a given value of h are partial derivatives, as are the rates of change of any of these variables with respect to h at a given time.

Partial differential equations are discussed at length in Chap VI. They are mentioned here only for contrast with ordinary differential equations and to emphasize the point that they arise only in those problems where there are two or more independent variables. The remainder of this chapter will be devoted to illustrations of the methods available for the formulation of ordinary differential equations.

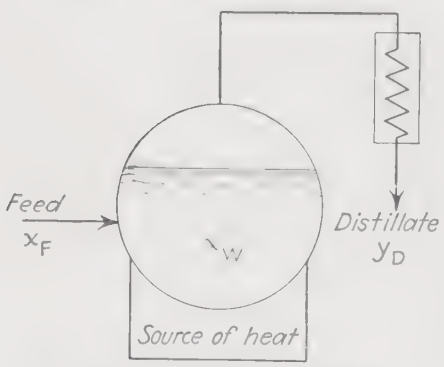


FIG. 17.—Batch distillation.

22. Differential Material Balances in Distillation. The use of differentials in setting up differential equations is well illustrated by those problems demanding the use of material balances. Consider, for example, the case of starting the equilibrium still shown schematically in Fig. 17. The still is purifying benzene and toluene from a small amount of essentially nonvolatile impurity and is initially charged with 20 lb. mols of feed stock of composition $x_F = 0.32$ mol fraction benzene. Feed is supplied at the rate of 10 lb. mols per hr., and the heat input is adjusted so that the total mols of liquid in the still remain constant at 20. It is desired to estimate the time required for the composition of overhead product y_D to fall to 0.40 mol fraction benzene. No liquid stock is removed from the still during this period.

During a short period of time $d\theta$, the distillation of benzene may be assumed to occur at a constant rate, and a material balance on benzene may be set up as follows:

$$\text{Input} = 10(0.32)d\theta$$

and since the total mols in the still remain constant

$$\text{Output} = 10y_D d\theta$$
$$\text{Accumulation} = d(20x_W) = 20dx_W$$

Substitution in the material balance gives

$$3.2d\theta - 10y_D d\theta = 20dx_W \tag{23}$$

$$d\theta = \frac{20dx_W}{3.2 - 10y_D} \tag{24}$$

The left-hand side of this equation may be integrated directly, but before the right-hand side may be integrated it must be reduced to a function of one variable, *i.e.*, y_D must be known as a function of x_W. In the present case, the result of any refluxing in the neck of the still will be neglected and y_D assumed equal to the composition of equilibrium vapor off the still. The relation between x_W and y_D is given by vapor-liquid equilibrium data frequently too complex to express in the form of an equation. If the relation is known, the right-hand side of (24) may be evaluated by the graphical procedure described in Chap. I. Benzene and toluene, however, may be assumed to follow Raoult's law, and the relative volatility α* may be taken as constant at an average value of 2.48.

Under these circumstances

$$y_D = \frac{2.48x_W}{1 + 1.48x_W} \tag{25}$$

* If y_a and y_b are the vapor compositions of the two components a and b and if x_a and x_b are the corresponding equilibrium liquid compositions, the relative volatility α is defined by the equation

$$\frac{y_a}{y_b} = \alpha\frac{x_a}{x_b}$$

which in the case of a binary reduces to $y_a/(1 - y_a) = \alpha[x_a/(1 - x_a)]$. When Raoult's law is obeyed, α is the ratio of the vapor pressures of the two components.

Substituting for y_D in (24) and simplifying give

$$d\theta = \frac{20dx_W}{3.2 - 20.1x_W} + \frac{29.6x_W dx_W}{3.2 - 20.1x_W} \tag{26}$$

The limits of integration are inserted by recalling that when $\theta = 0$, $x_W = x_F = 0.32$, and when $\theta = \theta$, x_W is obtained as 0.21 by substitution of $y_D = 0.40$ in (25).

$$\theta = 20\int_{0.32}^{0.21} \frac{dx_W}{3.2 - 20.1x_W} + 29.6\int_{0.32}^{0.21} \frac{x_W dx_W}{3.2 - 20.1x_W} \tag{27}$$

Integration gives

$$\theta = \frac{-20}{20.1}\left[\ln (3.2 - 20.1x_W)\right]_{0.32}^{0.21} - 29.6\left[\frac{x_W}{20.1} + \frac{3.2}{(20.1)^2}\ln (3.2 - 20.1x_W)\right]_{0.32}^{0.21}$$

Substitution of limits gives

$$\theta = \frac{-20}{20.1}(2.3)\log\frac{3.2 - 20.1(0.21)}{3.2 - 20.1(0.32)} - 29.6\left[\frac{0.21 - 0.32}{20.1} + \frac{3.2}{(20.1)^2}(2.3)\log\frac{3.2 - 20.1(0.21)}{3.2 - 20.1(0.32)}\right]$$

$$= 1.58 \text{ hr.}$$

It is important to lay emphasis upon the general procedure to be followed in setting up a differential material balance such as (23). No difficulty will be experienced with regard to signs of differentials if the general rule is followed of substituting the differential input, output, and accumulation directly into the material balance

$$\text{Input} - \text{output} = \text{accumulation}$$

if no attention is paid to the inherent sign of the differentials themselves, and if they are always considered positive. For example, x_W in the preceding problem decreases as θ increases, so that dx_W is *inherently* negative when $d\theta$ is positive. In (23), however, it must be noted that the signs in front of all the differentials are taken as positive, the one negative sign always being present before the output term in the material balance when output is written on the left-hand side of the equation.

23. Use of Differential Energy Balance. Many processes involve the solution of a differential equation that represents a differential energy balance. It will be seen from the following illustration that the principles involved in setting up differential energy balances and differential material balances are identical.

A gas containing an entrained mist of nonvolatile tar is to be removed from an apparatus at 0.33 atm. and discharged to a tank at 1.0 atm. by means of an adiabatic reciprocating pump. The gas mixture contains 0.2 lb. tar per lb. tar-free gas and enters the pump at 170°F. Although the gas may be considered perfect over the range of temperatures and pressures involved, the tar mist, which may be considered to be always at the temperature of the gas, has a heat capacity of 0.5 B.t.u. per lb. and exerts a cooling effect during the compression, thereby lowering the amount of work required compared to that for the adiabatic compression of a perfect gas alone between the same two pressures. The heat capacity of the gas at constant volume is 6.2 B.t.u. per lb. mol, and its average molecular weight is 24. Displacement of the compressor is 0.4 cu. ft. It is desired to calculate the minimum quantity of work that must be supplied to the compressor during the compression stroke of the cycle.

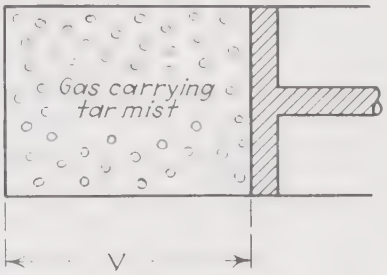


FIG. 18.

By an energy balance, the work supplied must be equal to the increase in internal energy of the gas and of the tar. At any point in the compression stroke (Fig. 18) let

v = volume of gas mixture, cu. ft.

p = pressure, lb. per sq. ft.

t = temperature, °F.

When the small volume of the tar is neglected, the weight of gas taken into the cylinder is calculated from the perfect gas laws as

$$0.40\left(\frac{492}{170 + 460}\right)0.33\left(\frac{24}{359}\right) = 0.0069 \text{ lb.}$$

The weight of tar supplied $= 0.2(0.0069) = 0.0014$ lb. Over a differential section of stroke, reversibility being assumed,

Work supplied $= p\,dv$

Increase in internal energy of gas $= 0.0069(6.2/24)dt$

Increase in internal energy of tar $= 0.0014(0.5)dt$

If the contents of the cylinder are taken as a system, the energy balance, or first law of thermodynamics as applied to this process, becomes

Change in internal energy of system = heat added to system − work done by system

When the first law is written with these signs, heat evolved by the system is considered negative and work done by the system is considered positive. Over a small portion of the compression stroke, the process may be assumed to occur under constant conditions and the first law expressed in the differential form

$$dI = dq - dw \tag{28}$$

$$dI = \left[0.0069\left(\frac{6.2}{24}\right) + 0.0014(0.5)\right]dt = 0.0025dt$$

Heat losses to the surroundings being neglected $dq = 0$, and (28) becomes

$$(778)0.0025dt = -p\,dv \tag{29}$$

where the number 778 is introduced to convert from B.t.u. to foot-pounds.

Before (29) may be integrated, one of the three variables must be eliminated. Since the vapor pressure of the tar is negligible, a relation between p and v is available in the perfect gas law

$$pv = \frac{W}{M}RT \tag{30}$$

where W = weight of v cu. ft. tar-free gas, lb.

M = average molecular weight of gas.

T = absolute temperature, °R. $= t + 460$.

R = gas law constant = 1,544 ft.-lb. per °R. per lb. mol.

Since nothing is yet known concerning the variation of v, and since the initial and final values of p are specified, it is best to replace dv by a term containing p and T.

Differentiating (30) gives

$$p\,dv = \frac{WR}{M}dT - v\,dp = \frac{WR}{M}dT - \frac{WRT}{Mp}dp \tag{31}$$

On substitution in (29) and collection of terms containing dp and dT

$$1.95dT = \frac{-WR}{M}dT + \frac{WRT}{Mp}dp \tag{32}$$

$$\left(1.95 + \frac{WR}{M}\right)\frac{dT}{T} = \frac{WR}{M}\frac{dp}{p} \tag{33}$$

Integration is between the limits of $T = T_1 = 630$ at $p_1 = 0.33$ atm. and $T = T_2$ at $p_2 = 1$ atm.

$$(1.95 + 0.44)\int_{630}^{T_2}\frac{dT}{T} = 0.44\int_{0.33}^{1}\frac{dp}{p} \tag{34}$$

The integral is

$$2.39 \ln \frac{T_2}{630} = 0.44 \ln 3 \tag{35}$$

$$T_2 = 630(3)^{\frac{0.44}{2.39}} = 772°\text{R}. \tag{36}$$

The required work w is now obtained by integrating (29) between $T_1 = 630$ and $T_2 = 772$

$$1.95\int_{630}^{772}dT = -\int_{0.40}^{v_2}p\,dv = -\int_{0}^{w}dw = -w \tag{37}$$

$$w = -1.95(772 - 630) = -277 \text{ ft.-lb.}$$

24. Summary of Steps in the Solution of a Problem Involving a Differential Equation. The preceding illustrations demonstrate the use of five well-defined steps in the solution of a problem involving differential equations.

1. Recall the basic physical laws that govern the situation, and decide which quantities must be regarded as unknown variables. If every quantity can be expressed in terms of a single independent variable, an ordinary differential equation may be expected.

2. Formulate the differential equation according to the physical laws in control.

3. Eliminate all but two variables from the equation formulated in 2. A thorough understanding of the physical situation should ensure no difficulty in these first three steps.

4. Obtain the general solution by suitable integration of the differential equation in two variables resulting from 3. This is primarily a mathematical problem.

5. Substitute the boundary conditions in the general solution, and determine the value of the constants for a particular solution applicable to the case at hand.

Steps 4 and 5 were combined in the two preceding illustrations since the boundary conditions were employed as the limits of integration. The same results would be obtained by evaluating each side of (29) and (33) as an indefinite integral and adding a constant of integration that could be evaluated by substitution of the boundary conditions.

The application of a differential material balance to a more complicated situation is illustrated by the following problem.

25. Concentration Gradient across a Bubble Plate. The usual calculations in the design of rectifying columns assume perfect mixing on each plate and that the composition of the liquid leaving the plate is the same as that of the liquid at every point on the plate. Actually, conditions as pictured by this simple concept do not exist on the plates in any real column. To study the effects of actual concentration gradients on the rectification of a binary mixture, it has been proposed to employ a column (Fig. 19) consisting of two horizontal rectangular perforated plates. Liquid reflux at its boiling point is to return from the condenser and flow from left to right across the second (upper) plate. The reflux leaving the right side of the second plate returns to the first (lower) plate, again flowing from left to right.

The two components A and B are miscible in all proportions, and their mixtures will be assumed to obey Raoult's law. Over the range of temperatures involved, the vapor pressure of A is just twice that of B so that the relative volatility of A to B, (α), is 2.00.

The column is to be operated at total reflux, *i.e.*, all the vapor passing up through the plates is condensed and returned as reflux. The still will be charged with liquid of such composition that when the steady state is reached the vapor entering the first plate will be of uniform composition (10 mol per cent A). For the purposes of the present calculation, we shall assume the plate efficiency to be 100 per cent at all points on the plates, *i.e.*, the vapor leaving the liquid at any point on the plates is in equilibrium with the liquid at that point. The vapors leaving the lower plate will be considered to be thoroughly mixed before

entering the top plate. It is required to calculate the average composition (mol per cent A) of the vapors leaving the top plate.

This composition may be readily calculated by suitable integration of differential material balances. The usual assumptions as

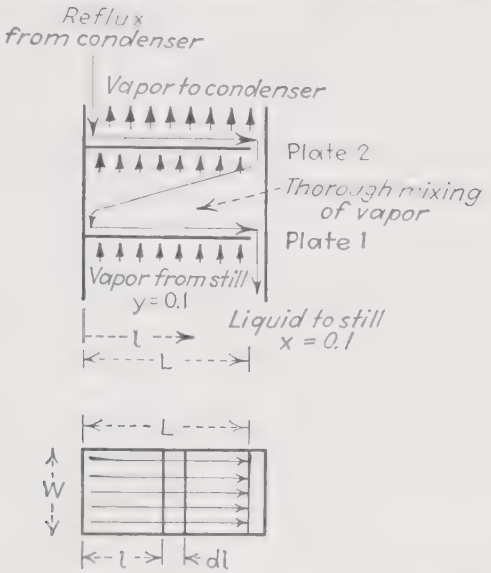


FIG. 19.—Rectifying column with cross down pipes.

to constancy of O and V will be made. The following nomenclature will be employed (see Fig. 19):

x_n = liquid composition at any point on nth plate (mol fraction).

y_n = composition of vapor evolved from any point on nth plate (mol fraction).

y_n^* = composition of vapor in equilibrium with liquid of composition x_n.

Y_n = composition of completely mixed vapor leaving nth plate.

l = distance from left to right on the plate.

L = length of plate.

W = width of plate.

V = mols of vapor flowing up column per unit width of plate.

O = mols of liquid flowing down column per unit width of plate.

Concentration gradients in the direction W will be neglected so that the actual value of W is immaterial and we may consider a plate simply one unit in width. Consider now a material

balance on component A over a differential length dl of the nth plate. Input of A in vapor to section from plate below $= (dl/L)Vy^*_{n-1}$. Input of A in liquid to section $= Ox_n$. Output of A in liquid from section $= O(x_n + dx_n)$. Output of A in vapor from section $= (dl/L)Vy^*_n$. The accumulation in the section is zero because the column is operating in the steady state.

Substitution into the material balance gives

$$\text{Input} - \text{output} = \text{accumulation}$$

$$\frac{dl}{L}Vy^*_{n-1} + Ox_n - O(x_n + dx_n) - \frac{dl}{L}Vy^*_n = 0 \tag{38}$$

When (38) is rearranged

$$\frac{V\,dl}{L}(y^*_n - y^*_{n-1}) = -Odx_n \tag{39}$$

On application of (39) to plate 1, y^*_{n-1}, the composition of vapor from the still, becomes constant at 0.1 and y^*_n is related to x_n by the equilibrium equation used previously

$$y^*_n = \frac{\alpha x_n}{1 + (\alpha - 1)x_n} = \frac{2x_n}{1 + x_n} \tag{40}$$

Substitution in (39) and separation of the variables result in

$$-\frac{(1 + x_1)dx_1}{1.9x_1 - 0.1} = \frac{V}{O}d\left(\frac{l}{L}\right) \tag{41}$$

When l varies from 0 to L, the variable l/L varies from 0 to 1. V/O is equal to unity because the column is operating at total reflux. Again, by a material balance, the composition of liquid leaving the first plate must be equal to 0.1, the composition of vapor rising from the still, and the composition of liquid entering the first plate must equal Y_1, the composition of mixed vapor leaving plate 1. Integrating between the limits of $x_1 = Y_1$, $l/L = 0$, $x_1 = 0.10$, $l/L = 1$, we obtain

$$\frac{1}{1.90}\left[2.30 \log (1.90x_1 - 0.10)\right]_{0.1}^{Y_1} + \left(\frac{x_1}{1.9}\right)_{0.1}^{Y_1} + \frac{0.1}{(1.90)^2}\left[2.30 \log (1.90x_1 - 0.10)\right]_{0.1}^{Y_1} = 1$$

Inserting the limits and collecting terms give

$$\frac{(2.00)(2.30)}{(1.90)^2} \log \left(\frac{1.90Y_1 - 0.1}{0.090}\right) + \frac{Y_1 - 0.10}{1.90} = 1 \tag{42}$$

Solution of (42) for Y_1 gives $Y_1 = 0.29$. Note that Y_1 is independent of the value of L. The next step is to apply the differential material balance (39) to plate 2.

$$\frac{V\,dl}{L}(y_2^* - Y_1) = -O dx_2 \tag{43}$$

Substitution for y_2^* in terms of x_2 from (40) and separation of the variables result in an equation exactly analogous to (41).

$$\int_{x_2=0.294}^{x_2=Y_2} \frac{(1 + x_2)dx_2}{1.71x_2 - 0.29} = \frac{V}{O}\int_{l=0}^{l=L} \frac{dl}{L} \tag{44}$$

Integration, substitution of limits, and solution for Y_2 in the preceding manner gives $Y_2 = 0.58 = x_{\text{condenser}}$.

26. Differential Heat and Material Balances Combined with a Heat-transfer Rate Equation—Concentration of KOH by Evaporation. A 10 per cent (by weight) solution of KOH is being concentrated to 25 per cent under a pressure of 1 atm. in a single-effect evaporator. As evaporation proceeds, no liquid is removed as such, but additional dilute solution is added so that the total weight of material present in the evaporator is always constant at 9,000 lb. When the concentration reaches 25 per cent, evaporation is discontinued, the concentrated solution discharged, and the evaporator charged anew with 10 per cent solution. The heating coils are set low enough to be submerged throughout the run, and saturated steam condensing at 244°F. is supplied to the steam chest. The over-all coefficient of heat transfer is 400 B.t.u./(hr.) (sq. ft.) (°F.) at the start and may be taken as proportional to the square of the over-all temperature difference between condensing steam and boiling solution. The area A of the heating surface is 600 sq. ft. It is desired to estimate the time required for the evaporation of one batch. The boiling point raising (B.P.R.) of KOH solutions at 1 atm. is given in Fig. 20. B.P.R. due to hydrostatic head will be

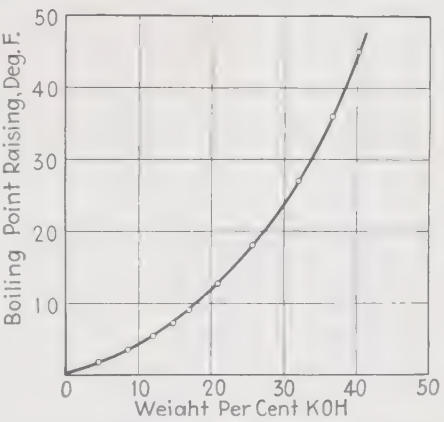


FIG. 20.—Boiling point raising of KOH solutions.

neglected. The latent heat of evaporation of water from the KOH solutions will be assumed constant over the range involved at 1000 B.t.u. per lb. water evaporated. Entering solution is at 210°F. and sensible heat effects will be neglected.

Let C = weight fraction of KOH in the evaporator at any time θ.

In time $d\theta$ the input of heat is $UA\ \Delta t\ d\theta$, and by a heat balance the weight of water evaporated is $UA\ \Delta t\ d\theta/1{,}000$ lb. The required differential equation may now be formulated by application of a water balance to the evaporator over the time interval $d\theta$. Since the weight of the evaporator contents (water plus solids) is to remain constant, the terms in the water balance are

$$\text{Input} = 0.9\frac{UA\ \Delta t\ d\theta}{1{,}000}$$

$$\text{Output} = \frac{UA\ \Delta t\ d\theta}{1{,}000}$$

$$\text{Accumulation} = d[9{,}000(1 - C)] = -9{,}000dC$$

Substituting in the material balance gives

$$0.9\frac{UA\ \Delta t\ d\theta}{1{,}000} - \frac{UA\ \Delta t\ d\theta}{1{,}000} = -9{,}000dC \tag{45}$$

When variables are collected,

$$d\theta = \left(\frac{9 \times 10^7}{A}\right)\frac{dC}{U\ \Delta t} \tag{46}$$

If the right-hand side of this equation is to be integrated analytically, all quantities must be expressed as a function of a single variable. It has been stated that U is proportional to $(\Delta t)^2$ so that U may be eliminated by placing $U = a(\Delta t)^2$ where a is a constant, the value of which must be determined from the fact that $U = 400$ at the start of evaporation, when $C = 0.1$. The known relation between Δt and C may be expressed by an approximate empirical equation, following the methods of Chap. VII, but it is doubtless more practical to resort to solution by graphical integration. When integrated between the limits of $\theta = 0$, $C = 0.1$ and $\theta = \theta$, $C = 0.25$, (46) becomes

$$\theta = \frac{900}{600a}\int_{c=0.10}^{c=0.25}\frac{10^5 dC}{(\Delta t)^3} \tag{47}$$

As indicated in Chap. I, the value of this integral is represented by the area under a curve of C vs. $10^5/(\Delta t)^3$ bounded by the

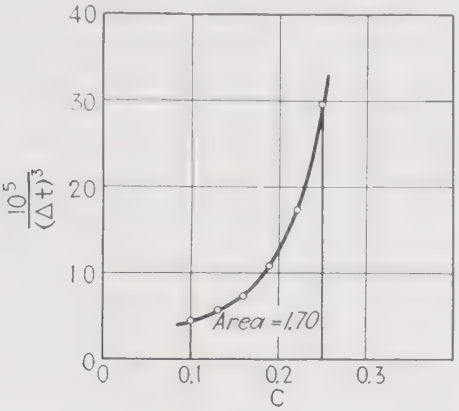


FIG. 21.

ordinates at $C = 0.25$ and $C = 0.1$. The necessary computations have been carried out in Table I and the required area determined

TABLE I.—COMPUTATIONS PRELIMINARY TO GRAPHICAL INTEGRATION

C	B.P.R.	$t_s(= 212 + \text{B.P.R.})$	$\Delta t(= 244 - t_s)$	$(\Delta t)^3$	$\frac{10^5}{(\Delta t)^3}$
0.10	4.3	216	28	22,000	4.5
0.13	6.1	218	26	17,500	5.7
0.16	8.3	220	24	13,800	7.2
0.19	10.8	223	21	9,270	10.8
0.22	13.8	226	18	5,830	17.1
0.25	17.4	229	15	3,380	29.6

as 1.7 (see Fig. 21). When $C = 0.1$, $\Delta t = 28$, and $U = 400$, whence

$$a = \frac{400}{(28)^2} = 0.51$$

Hence

$$\theta = \frac{900}{600(0.51)}(1.7) = 5.0 \text{ hr.}$$

27. Rate Equations. As pointed out in Chap. I, the fundamental laws governing each of the unit operations in chemical engineering are most readily expressed in the form of simple rate equations. In heat transmission by conduction, for example, the basic law states that the rate of heat transmission with

respect to time, $dQ/d\theta$, is directly proportional to the area normal to the direction of flow and to dt/dx, the rate of change of temperature with distance in the direction of flow. The basic law in the theory of viscous flow in pipes states that in a given pipe the rate of change of pressure with length of pipe is proportional to the velocity of flow. Diffusion theory proceeds from the basic law that the rate of mass transferred by diffusion with respect to time is directly proportional to the area normal to the direction of flow and to dc/dx, the rate of change of concentration with distance in the direction of flow. The rate at which a chemical reaction proceeds is a function of the concentrations of the reacting substances.

In view of the fact that the mathematical statements of all of the preceding laws and many others not mentioned are essentially parallel, it is not surprising to find that the underlying quantitative treatment of many unit operations is quite similar. Particular cases, however, demand the combination of these simple rate equations with differential material and energy balances in such an endless variety of combinations that the various integrated equations often bear but superficial, if any, semblance to each other. The following problems have been selected for the purpose of illustrating the methods of combining these simple relationships in the solution of more complex problems.

28. Diffusion Combined with Chemical Reaction. Rate Equation Combined with Differential Material Balance. A gas is absorbed by a solution with which it reacts chemically. The reaction is slow, and rate of diffusion of the gas through the liquid controls the absorption process. The rate of diffusion in the liquid will be assumed proportional to the concentration gradient, and the diffusing gas is eliminated as it diffuses by a chemical reaction of the first order in which the rate of reaction is proportional to the concentration of the solute gas in the liquid. It is required to obtain an expression for the concentration in the liquid as a function of the distance from the interface.

Although no new principles are involved in formulating the differential equation arising from this problem, it will be convenient to illustrate the use of a slightly different technique which has general applicability in cases of this nature.

Figure 22 represents an enlarged section of the liquid film adjacent to the gas-liquid interface. Conditions at any point in a

plane a distance x from the interface and normal to the direction of diffusion are the same, and a material balance will be set up describing the diffusion in and out of the differential element of thickness dx. Considering the diffusion across one unit of area into this differential layer, we have as the rate of input of material

$$\text{Rate of input} = -D\frac{dc}{dx} \tag{48}$$

where D is the diffusion constant and c the concentration of gas in the liquid at the point x. Since the concentration gradient is inherently negative in the direction of flow, it is necessary to place a negative sign before the gradient in order to substitute with no change of signs into the material balance as ordinarily written.

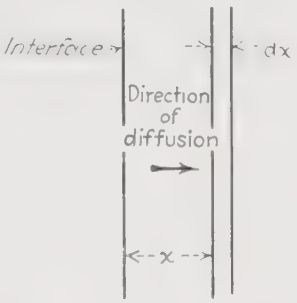


FIG. 22.

The input of material during the time $d\theta$ is given by the product of rate of input and time.

$$\text{Input} = -D\frac{dc}{dx}d\theta \tag{49}$$

As x undergoes the change dx, the concentration gradient changes by $d(dc\ dx)$ and at the other boundary of the layer has become $(dc/dx) + d(dc/dx)$.

The output from the element across unit area is again given by the diffusion law during time $d\theta$ as

$$\text{Output} = -D\left[\frac{dc}{dx} + d\left(\frac{dc}{dx}\right)\right]d\theta \tag{50}$$

While diffusion is taking place across the layer dx, the diffusing material disappears by chemical reaction at a rate proportional to the amount of material present. The volume of the element under consideration is dx since unit area is being considered, and the quantity of diffusing material in the element at any time is given by the product of this volume and the concentration c. The rate of chemical reaction is $d(c\ dx)/d\theta$ and

$$-\frac{d(c\ dx)}{d\theta} = kc\ dx \tag{51}$$

where k is the reaction-rate constant.

There may appear to be some question regarding the validity of the differential method in setting up an equation involving a

term such as $d(dc/dx)$, which leads eventually to a second derivative. No error has been made, however, as dc/dx is itself a variable, and in (50) we are merely introducing the first differential of this function in an orthodox manner.

The quantity of diffusing material disappearing by chemical reaction in the element in time $d\theta$ is

$$\text{Output} = \frac{-d(c\,dx)}{d\theta}d\theta = kc\,dx\,d\theta \tag{52}$$

If we focus attention on the material diffusing it becomes evident that the quantity (52) may be considered as output. Since diffusion is taking place under steady-state conditions there is no accumulation, and the material balance becomes

$$-D\frac{dc}{dx}d\theta + D\left[\left(\frac{dc}{dx}\right) + d\left(\frac{dc}{dx}\right)\right]d\theta - kc\,dx\,d\theta = 0 \tag{53}$$

Division by $d\theta \cdot dx$ and collection of terms give

$$\frac{d}{dx}\left(\frac{dc}{dx}\right) = \frac{k}{D}c \tag{54}$$

But the left-hand side of (54) is in reality a second derivative, and we have as the final differential equation relating c and x

$$\frac{d^2c}{dx^2} = \frac{k}{D}c \tag{55}$$

This is a linear differential equation of the second order and has a well-known solution, which will be discussed in Chap. III.

A little practice enables one to set up equations of this type with the omission of several of the preceding detailed steps. More involved cases, however, usually demand recourse to the detailed method which has been given.

29. Flow of Heat from a Fin — Rate Equation Combined with Differential Heat Balance. Comparison of this case with the preceding problem on absorption followed by chemical reaction will serve to illustrate the mathematical similarity between entirely different physical situations.

A metallic fin shown in section in Fig. 23 is supported between two heat sources 1 ft. apart so that one end is held constant at 200°F. and the other constant at 100°F. The fin is of copper [k = 220 B.t.u. (ft.)/(hr.)(sq. ft.)(°F.)] and is a flat strip 0.1 in.

thick, of perimeter P ft. and cross section A sq. ft. The over-all surface coefficient U, defined with respect to the temperature difference between the surroundings and the surface of the fin, may be assumed constant at 2.0 B.t.u./(hr.)(sq. ft.)(°F.). The surroundings are at 0°F. It is desired to obtain a relation between the temperature of the fin at any point and the distance of this point from the hot end.

Strictly speaking, it may be seen that the solution of this problem involves a partial differential equation since the temperature is not exactly constant across any cross section of the fin but is a function of the distance x and the distance from the surface of the fin. However, the fin is so thin and the conductivity of the metal of which it is composed is so great that we may, without appreciable error, neglect temperature gradients in the vertical

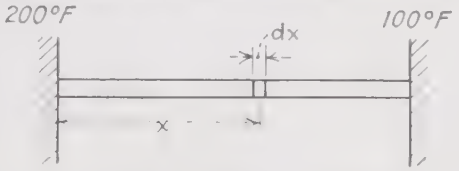


FIG. 23.—Heat conduction in flat metal fin.

direction and assume the temperature constant over any cross section normal to the x axis. The only heat flow of any consequence is that in the x direction. It follows that the temperature is constant at all points on any cross section normal to this direction and is a function of one independent variable x. Under these circumstances, the temperature distribution may be described by an ordinary differential equation.

Consider the flow of heat into an element of thickness dx at any distance x from the hot end. The rate of heat flow into the element is given by the fundamental equation of conduction as

$$\frac{dQ}{d\theta} = -kA\frac{dt}{dx} \tag{56}$$

Q being the quantity of heat that has crossed a plane normal to the direction of flow at a distance x from the origin in time θ.

The quantity of heat entering the element in time $d\theta$ is

$$\frac{dQ}{d\theta}d\theta = -kA\frac{dt}{dx}d\theta \tag{57}$$

As x undergoes the change dx, the temperature gradient undergoes the change $d(dt\ dx)$. The change in the gradient is then

its rate of change with respect to x multiplied by the change in x, so that

$$d\frac{dt}{dx} = \frac{d\frac{dt}{dx}}{dx}dx = \frac{d^2t}{dx^2}dx \tag{58}$$

Heat flow from the element in the direction x is then

$$-kA\left(\frac{dt}{dx} + \frac{d^2t}{dx^2}dx\right)d\theta \tag{59}$$

Heat lost from the element to the surroundings at temperature t_s in time $d\theta$ is

$$UP\,dx(t - t_s)d\theta \tag{60}$$

As the fin is operating under steady-state conditions, there is no accumulation of heat in the element and a heat balance on the element must state that heat input by conduction from fin = heat output by conduction to fin plus heat lost to surroundings. Substitution of (57), (59), and (60) into the heat balance gives

$$-kA\frac{dt}{dx}d\theta = -kA\left(\frac{dt}{dx} + \frac{d^2t}{dx^2}dx\right)d\theta + UP\,dx(t - t_s)d\theta \tag{61}$$

Division by $d\theta \cdot dx$ and collection of terms lead to

$$\frac{d^2t}{dx^2} = \frac{UP}{kA}(t - t_s) \tag{62}$$

Equation (62) is identical with (55) since in the present case $t_s = 0$, and, even though the two cases are physically different, the mathematical problems involved are the same. Mathematically parallel cases of this nature are found to occur frequently throughout the study of unit operations

30. Simultaneous Processes Occurring As a Function of a Single Variable. Estimation of Breathing Losses from a Benzol Storage Tank. It is not uncommon to find several different processes occurring as a result of a change in one variable, each of these processes making a contribution to the corresponding change in the quantity of interest. In such cases, a differential analysis permits the calculation of the differential changes in the quantity of interest due to each process, and the sum of these differential changes may be integrated to give the final result.

A simple illustration of this principle develops in the analysis of breathing losses from a storage tank.

The tank, 30 ft. in diameter, is filled with liquid benzol to a depth of 9 ft. The gas space above the benzol has a volume V_0 of 8,660 cu. ft. and is connected with the outside atmosphere by a vent pipe. The maximum and minimum daily temperatures are 100° and 50°F., respectively (barometric pressure may be taken as 760 mm. Hg), and it is desired to obtain an estimate of the maximum possible breathing losses per day. The partial pressure of benzol may be calculated from the equation

$$\log_{10} p = 7.962 - \frac{1,781}{T}$$

where p is in mm. Hg, and T is in °K.

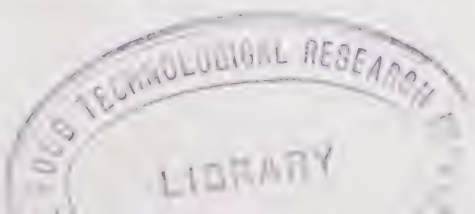
Loss of benzol occurs when the benzol-air mixture in the gas space receives heat from the surroundings, expands, and is driven out the vent pipe into the atmosphere to be blown away. When the temperature falls, the benzol-air mixture contracts, and fresh air is drawn into the gas space only to be reexpelled with a certain benzol content when the temperature rises.

In the absence of any internal heat supply, the maximum benzol loss will occur when the gas leaving the vent pipe contains the maximum possible benzol it can carry at the temperature of the surroundings. This condition implies that the air above the liquid benzol must be always saturated with benzol vapor at the temperature of the surroundings.

The benzol loss is the result of two processes occurring simultaneously, each causing an increase in volume of gas above the benzol. First, the gas already present undergoes simple thermal expansion according to the gas law, the increase in volume being dV_T where

$$dV_T = V_0 \frac{dT}{T}$$

The second process acting to increase the volume is the incremental vaporization of benzol necessary to keep the gas space saturated at $T + dT$ in accordance with the condition necessary for maximum loss. If y is the mol fraction of benzol in the gas space at any time, the total volume of benzol present in the gas space (reckoned at the total pressure) is yV_0, and, when the gas composition changes as a result of saturation at a higher tem-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perature, the necessary vaporization of benzol dV_y amounts to $d(yV_0) = V_0\,dy$. The total volume of benzol-saturated air lost out the vent pipe as a result of temperature change dT is the sum of the differential increases in volume due to thermal expansion and benzol vaporization. Denoting this total increase in volume by dV, we have

$$dV = dV_T + dV_y = V_0\left(\frac{dT}{T} + dy\right) \tag{63}$$

The change in liquid volume is negligible in comparison with the total gas volume, and V_0 may be considered constant throughout the process. The mol fraction of benzol y is $p/760$, where p is the partial pressure of benzol at T and

$$dy = \frac{dp}{760}$$

Equation (63) then becomes

$$dV = V_0\frac{dT}{T} + V_0\frac{dp}{760} \tag{64}$$

This equation could be integrated directly to give the total volume of gas expelled from the tank as a result of the 50°F. rise in temperature, but the benzol loss would still present a problem in calculation since this volume of gas is made up of an infinite number of differential volumes each saturated with benzol at the variable temperature at which it was driven from the vent pipe. It is therefore necessary to derive an expression for dN, the pound mols of benzol carried out by dV cu. ft. of benzol-saturated air. This relation follows directly from the gas laws and is

$$dN = \frac{p\,dV}{RT} \tag{65}$$

Consistent units must be used in this equation. In English units, $R = 1{,}544$ and

$$dN = \left(\frac{p}{760}\right)\frac{(14.7)(144)dV}{(1{,}544)(T)1.8} = (0.001)\frac{p}{T}dV \tag{66}$$

where N is in lb. mols, p is in mm. Hg, V is in cu. ft., and T is in °K. Substituting this value of dN in (64) and placing

$$V_0 = 8{,}660 \text{ cu. ft.},$$

we have

$$dN = (0.001)\frac{p}{T}dV = 8.66\left(\frac{p\,dT}{T^2} + \frac{p\,dp}{760T}\right) \tag{67}$$

The relation between p and T as already given when solved for p becomes

$$p = e^{2.3\left(7.962-\frac{1,781}{T}\right)} \tag{68}$$

and when solved for $1/T$ becomes

$$\frac{1}{T} = \frac{7.962 - \frac{\ln p}{2.3}}{1,781} \tag{69}$$

Substituting in (67) for p and $1/T$ results in

$$dN = 8.66\left[e^{2.3\left(7.962-\frac{1,781}{T}\right)}\frac{dT}{T^2} + \frac{p}{(760)(1,781)}\left(7.962 - \frac{\ln p}{2.3}\right)dp\right]$$

Integrating between the limits of $T_1 = 283°$K. and $T_2 = 310.8°$K. and the corresponding values of p obtained from (68), we have

$$N = \frac{8.66}{(2.3)(1,781)}\left[e^{2.3\left(7.962-\frac{1,781}{T}\right)}\right]_{T_1=283}^{T_2=310.8} - \frac{0.0114}{1,781(2.3)}\left[p^2\left(\frac{\ln p}{2} - \frac{1}{4}\right)\right]_{p_1}^{p_2} + \frac{0.0114(7.962)}{1,781(2)}\left[p^2\right]_{p_1}^{p_2}$$

Substitution of limits results in a value of N of 0.77 lb. mols per day. The molecular weight of benzene being 78, this is the equivalent of 78(0.77) = 60 lb.

31. The General Rate Equations for Homogeneous Chemical Reactions. Consider the general irreversible reaction

$$aA + bB + cC \rightarrow dD + eE + fF \tag{70}$$

where a denotes the mols of species A reacting with b mols of B and c mols of C and where the mechanism of reaction is exactly as indicated by the stoichiometrical formulation. In deriving an expression for the rate of reaction, it is immaterial whether one follows the rate of *disappearance* of any molecular species on the left or the rate of *appearance* of any molecular species on the right. For purposes of illustration, we shall follow the rate of disappearance of species A. At any time θ, let N_A represent the

mols of A present so that $dN_A/d\theta$ will represent the mols of A disappearing per unit time. As θ increases, N_A decreases so that if $dN_A/d\theta$ is to be equated to quantities inherently positive it must be preceded by a negative sign. $dN_A/d\theta$ is first of all proportional to N_A, the mols of A present at any time, because clearly, if N_A is doubled, twice as many molecules will be available for reaction, resulting in double the number of mols disappearing per unit time; insertion of N_A is in reality insertion of a factor to allow for the scale of the operation. Reaction (70) may be written

$$(1)A + (a - 1)A + bB + cC \rightarrow dD + eE + fF \qquad (71)$$

Focusing attention upon one molecule of A (71) makes it clear that for reaction to occur this molecule must collide simultaneously with $(a - 1)$ molecules of A, b molecules of B, and c molecules of C. The rate of disappearance of A is proportional to the number of simultaneous collisions of the type just mentioned, and the number of these collisions is proportional to the product of the concentrations of the reacting molecules, the concentration of each species being raised to a power corresponding to the number of molecules of that species which must collide with the molecule of A under consideration. The differential equation expressing the rate of disappearance of A at constant temperature is then

$$\frac{dN_A}{d\theta} = -kN_A C_A^{a-1} C_B^b C_C^c \qquad (72)$$

where C represents concentration as mols per unit volume.

Equation (72) is the *general* equation applying to reaction rate in homogeneous systems.

The initial quantities of all species concerned in the reaction being known, it is possible by use of material balances, together with the stoichiometrical relations involved, to express all concentrations as functions of N_A; and the two variables N_A and θ, together with their differentials, may then be collected to give a solution of (72) by simple integration.

In the case of an adiabatic reaction, the temperature of the reacting materials will vary, and k, being a function of temperature, will vary. It is possible by application of an enthalpy balance,* knowing the enthalpy of reaction and the heat capaci-

* Known often as a "heat content" or heat balance.

ties of the substances concerned, to express the temperature of reaction as a function of N_A and hence to obtain k as a function of N_A. Under these circumstances, procedure by analytical methods is usually impractical, and it is best to write (72) in the form

$$\int_0^\theta d\theta = \int_{N_{A_0}}^{N_A} \frac{-dN_A}{kN_A C_A^{a-1} C_B^b C_C^c} \tag{73}$$

and evaluate graphically. In a reaction occurring at constant pressure under flow conditions and involving a change in volume, the time of contact θ may be a function of N_A. An example of this kind is given in Par. 33. In the special case of reaction at constant volume V, since $C_A = N_A/V$ and $dN_A = V\,dC_A$, Eq. (72) reduces to

$$\frac{dC_A}{d\theta} = -kC_A^a C_B^b C_C^c \tag{74}$$

Equation (74) is the form of the reaction-rate law usually seen in textbooks on physical chemistry. Obviously it is not generally applicable to the industrially important case of reaction at constant pressure unless there is no change in total mols, a condition implying constant volume.

By application of the stoichiometrical relations between the reactants and products given by (70), (72) is readily transformed to apply to any one of the molecular species present. For example, we can follow the appearance of D by substituting in (72) the relation

$$-dN_A = \frac{a}{d} dN_D \tag{75}$$

whereupon (72) becomes

$$\frac{dN_D}{d\theta} = k\left(\frac{d}{a}\right) N_A C_A^{a-1} C_B^b C_C^c \tag{76}$$

In the application of equations of the type of (74) and (76), complication may arise from several sources. First of all, the general reaction represented by (70) may be reversible, in which case species A is being consumed by the forward reaction and generated by the reverse reaction. To follow the net change in quantity of any species with time, (72) must be applied to both forward and reverse reactions.

A frequent complication arises when the mechanism of the reaction may not be the same as indicated by the stoichiometric formulation. There may be intermediate products formed and subsequently broken down to the final products. In this case, the rate equation is written for the controlling reaction and substitution of terms based on the over-all stoichiometry.

Finally, it is possible for the reactants as well as the intermediate products to be consumed by many side reactions in addition to the main reaction. If the quantity of material affected by these side reactions is appreciable, unless their nature is known, the development of a quantitative description of rate of conversion of any of the reactants must proceed on an empirical basis.

32. Consecutive Reversible Reactions at Constant Volume. As an example of a case not often presented, let us consider the set of reversible reactions

$$A \rightleftarrows B \qquad (a)$$
$$B \rightleftarrows C \qquad (b)$$

Assume 1 mol of A present at the start, and let x, y, and z denote the mols of A, B, and C, respectively, present at time θ. Then, since the reaction is assumed to occur at constant volume, x, y, and z are proportional to concentrations. Let k_1 and k_2 be the velocity constants of the forward and reverse reactions, respectively, of (a); likewise, let k_3 and k_4 apply to (b). The net rate of disappearance of A is given by application of (74) to the forward and reverse reactions (a)

$$\frac{dx}{d\theta} = -k_1 x + k_2 y \qquad (77)$$

and the net rate of disappearance of B is given by

$$\frac{dy}{d\theta} = -(k_2 + k_3)y + k_1 x + k_4 z \qquad (78)$$

At all times, the material balance and the stoichiometrical relations dictate the relation

$$x + y + z = 1$$

Differentiate (77) with respect to θ.

$$\frac{d^2x}{d\theta^2} = -k_1 \frac{dx}{d\theta} + k_2 \frac{dy}{d\theta} \qquad (79)$$

Substitute $dy/d\theta$ from (78).

$$\frac{d^2x}{d\theta^2} = -k_1\frac{dx}{d\theta} - k_2(k_2 + k_3)y + k_2k_1x + k_2k_4z \qquad (80)$$

Replacing z by its value $(1 - x - y)$, substituting y from (77), and collecting terms give

$$\frac{d^2x}{d\theta^2} + (k_1 + k_2 + k_3 + k_4)\frac{dx}{d\theta} + (k_1k_3 + k_2k_4 + k_1k_4)x - k_2k_4 = 0 \qquad (81)$$

This is a linear equation with constant coefficients and is solved in Chap. III. The solution gives the relation between x and θ.

33. Chemical Reaction in a Flow System under Constant Pressure. In the application of (72) to a reaction carried out isothermally under flow conditions at constant pressure and involving a change in volume, an additional complication arises owing to the fact that the reaction time of contact θ is a function of the extent to which reaction has occurred. The following problem is typical of the method of treatment.

For the kinetically second-order irreversible decomposition of acetaldehyde

$$2CH_3CHO \rightarrow 2CH_4 + 2CO \qquad (82)$$

Hinshelwood and Hutchison* report

$$k = 0.331/(\text{sec.})\ (\text{g. mols per l.}) \text{ at } 518°C.$$

Assume this reaction to be carried out at 1 atm. by boiling the aldehyde in a flask and introducing the vapors into one end of a silica reaction tube while withdrawing products from the other end. All the contents of the reaction tube will be maintained at 518°C. If the reaction tube is 3.3 cm. internal diameter and 80 cm. long, and if aldehyde is introduced at the rate of 50 g. per hr., what fraction of the aldehyde distilled will be decomposed?

As a basis for calculation, consider the continuous introduction into the reaction tube of N_{A_0} mols of aldehyde per unit time and let N_A represent the mols of aldehyde undecomposed after any time of reaction θ per N_{A_0} mols of original aldehyde. Application of (72) to (82) then gives

$$\frac{dN_A}{d\theta} = -kN_AC_A \qquad (83)$$

* *Proc. Roy Soc.* A, 111,380 (1926).

The problem is now the elimination of one of the variables from (83) so that integration may proceed. However, it is convenient to replace two of the variables C_A and θ by V_R, the variable volume of the reaction tube.

Let V be the volume of undecomposed aldehyde plus decomposition products corresponding to the value of N_A after any time of reaction. From the stoichiometry of (82) and by assumption of the perfect gas laws,

$$V = \frac{RT}{p}[N_{A_0} + (N_{A_0} - N_A)] \tag{84}$$

Figure 24 is a diagram of the reaction tube. If x is the distance of any point from the entrance of the tube, then the volume

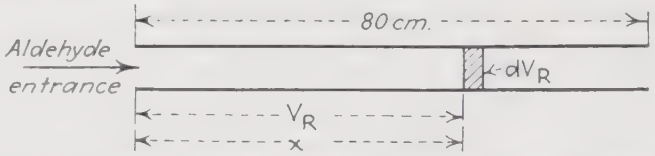

FIG. 24.—Chemical change in reaction tube at constant pressure.

V_R of the tube up to point x is Ax, where A is the cross-sectional area of the tube. Consequently

$$dV_R = A\,dx$$

Uniform velocity of the vapor at any cross section being assumed, the velocity u of a small mass of gas traveling a distance dx in the time $d\theta$ becomes

$$u = \frac{dx}{d\theta} = \frac{dV_R}{A\,d\theta} = \frac{V}{A} \tag{85}$$

whence

$$d\theta = \frac{A}{V}dx = \frac{dV_R}{V} \tag{86}$$

V is the volume of material resulting from the introduction into the reaction tube of N_{A_0} mols of aldehyde per unit time and may be visualized as the volume per unit time passing any point x (Fig. 24). The time of contact of the slug of gas V for reaction in the differential volume dV_R is $d\theta$.

Equation (86) relates the time of reaction contact in the tube θ to the volume of the tube V_R and recalls the discussion in Par. 21.

It remains to express C_A in terms of N_A. This may be accomplished by recalling that the definition of concentration is

$$C_A = \frac{N_A}{V} = \frac{N_A p}{RT(2N_{A_0} - N_A)} \tag{87}$$

Substitution of (86) and (87) in (83) gives

$$\frac{dN_A}{dV_R} = \frac{-kN_A^2}{V^2} = -k\left(\frac{p}{RT}\right)^2\left(\frac{N_A}{2N_{A_0} - N_A}\right)^2 \tag{88}$$

Separation of the variables leads to

$$\left(\frac{4N_{A_0}^2}{N_A^2} - \frac{4N_{A_0}}{N_A} + 1\right)dN_A = -k\left(\frac{p}{RT}\right)^2 dV_R \tag{89}$$

Since the problem asks for the fraction of aldehyde decomposed when $V_R = 80\frac{\pi}{4}(3.3)^2$ cc., the volume of the reaction tube, it is convenient to let $N_A/N_{A_0} = f$, the fraction undecomposed, whereupon $dN_A = N_{A_0}\,df$, and (89) becomes

$$N_{A_0}\left(\frac{4}{f^2} - \frac{4}{f} + 1\right)df = -k\left(\frac{p}{RT}\right)^2 dV_R \tag{90}$$

Integration of (90) between the limits of $f = 1$, $V_R = 0$ and of $f = f$, $V_R = V_R$, the small change in p through the tube due to friction being neglected, gives

$$4 - \frac{4}{f} - 4\ \ln f + (f - 1) = \frac{-k}{N_{A_0}}\left(\frac{p}{RT}\right)^2 V_R \tag{91}$$

For a given input of aldehyde per unit time N_{A_0}, (91) makes possible the calculation of f, the fraction undecomposed after passage through a reaction tube of volume V_R.

In computing a value of f from (91), consistent units must be used throughout. Thus, if the c.g.s. system is used,

$$k = 0.331/(\text{sec.})(\text{g. mols per l.})$$

$$N_{A_0} = \frac{50}{3{,}600(44)} = 3.16 \times 10^{-4}\ \text{g. mol per sec.}$$

$$p = 1\ \text{atm.}$$

$$T = (518 + 273) = 791°\text{K.}$$

$$R = 0.08206\ \text{l. atm./(g. mol)(°K.)}$$

$$V_R = \frac{\pi(3.3)^2(80)}{(4)1{,}000} = 0.683\ \text{l.}$$

$$-\frac{k}{N_{A_0}}\left(\frac{p}{RT}\right)^2 V_R = \frac{-(0.331)}{3.16 \times (10^{-4})}\left(\frac{1}{(0.08206)(791)}\right)^2(0.683) = -0.17$$

$$3 - \frac{4}{f} - 9.2 \log f + f = -0.17$$

Solution by trial gives $f = 0.87$; and 13 per cent of the aldehyde will be decomposed upon passage through the tube.

34. Determination of the Order of a Chemical Reaction. The analysis of experimental data to determine the order of a chemical reaction involves, primarily, only stoichiometry and the rate equations, but the more complex cases frequently require considerable ingenuity. The usual procedure is to compare the data with integrated rate equations based on several possible reaction mechanisms. The test may be made graphically or may be based on the relative constancy of the reaction-rate constants calculated from the data on the basis of several hypotheses as to the reaction mechanism. The graphical tests usually involve finding some method of plotting the data that would give a straight line if the assumed mechanism were the correct one. In many cases, it is impossible to *prove* what the mechanism really is, although it may be possible to show that the data are compatible with but one of several mechanisms that appear to be reasonable in view of the known chemistry of the reacting substances.

Most experiments carried out to study the nature of a reaction are performed at constant volume and temperature, and the rate equation is of the form (74). In the case of an irreversible first-order reaction of the type

$$A \rightarrow B$$

the rate equation for constant volume reduces to

$$\frac{dC_A}{d\theta} = -kC_A$$

whence

$$\ln \frac{(C_A)}{(C_A)_0} = -k\theta \tag{92}$$

where $(C_A)_0$ is the initial concentration of the reacting material A. This equation suggests a plot of C_A vs. θ on semilogarithmic coordinate paper as a test of a first-order mechanism. Since constant volume is assumed, C_A may be replaced by the fraction A undecomposed as ordinate. The disintegration of radium is a classical example of a first-order reaction.

Figure 25 shows the data of Kruyt on the decomposition of phosphine plotted as fraction undissociated vs. time on semilogarithmic coordinate paper for the purpose of testing the

possibility of a first-order reaction. The resulting straight line indicates that the reaction is of this type, although the equation

$$4PH_3 = P_4 + 6H_2$$

suggests that a fourth order might be expected. This result emphasizes the point that the chemical equation merely indicates the stoichiometry of an over-all process that may be the result of a series of several reactions, any one of which may be controlling from the point of view of rate.

In studying reactions of gases, the quantity measured is frequently the total pressure rather than the composition of the gas mixture, and it is convenient to introduce this variable into

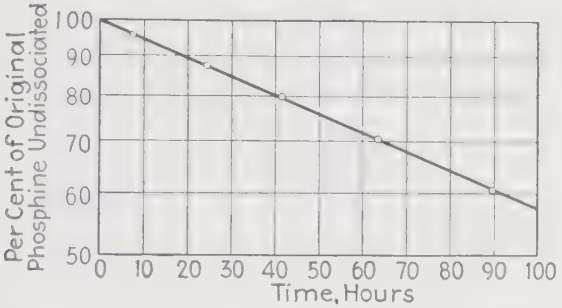

FIG. 25.—Decomposition of phosphine.

the rate equation, using the stoichiometry of the over-all process. The following data are reported by Hinshelwood and Burk* for the constant-volume decomposition of nitrous oxide at 757°C.:

Time (sec.)	0	15	30	50	98
Total pressure (mm. Hg)	258	268	278	288	308

The chemical reaction is

$$2N_2O \rightarrow 2N_2 + O_2$$

showing that 3 mols of gas are formed for every 2 mols of N_2O decomposed. If p_0 represents the initial pressure and p the pressure at time θ, then the concentration of N_2O is given by

$$C = \frac{N}{V} = \frac{[p_0 - 2(p - p_0)]}{RT} = \frac{3p_0 - 2p}{RT}$$

If the reaction is second order, then

$$\frac{dC}{d\theta} = -kC^2$$

* *Proc. Roy. Soc.*, **106**A, 384 (1924).

whence

$$-\frac{2}{RT}\frac{dp}{d\theta} = -\frac{k}{R^2T^2}(3p_0 - 2p)^2$$

which may be integrated to give

$$\frac{1}{3p_0 - 2p} - \frac{1}{p_0} = \frac{k\theta}{RT} \tag{93}$$

The applicability of this form may be tested by calculating values of k/RT, as shown in the following table:

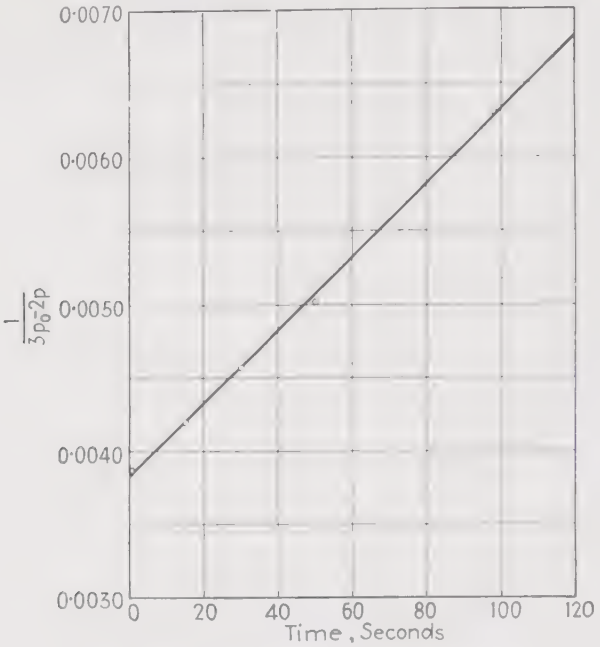

FIG. 26.—Dissociation of nitrous oxide.

TABLE II

θ	p	$\frac{1}{3p_0 - 2p}$	$\frac{k}{RT}$
0	258	0.00387	
15	268	0.00420	0.000022
30	278	0.00458	0.000024
50	288	0.00504	0.000023
98	308	0.00632	0.000025

The values of k/RT are constant within the probable accuracy of the data, and the assumption of a second order is substantiated.

An alternate test is a graph of $1/(3p_0 - 2p)$ vs. θ, since (93) is linear. The points are shown on Fig. 26 and fall practically on a straight line.

As another example we may analyze the following data of Smith* on the constant-volume dissociation of sulfuryl chloride at 279.2°C.:

Time (min.)	3.4	15.7	28.1	41.1	54.5	68.3	82.4	96.3
Total pressure (mm. Hg)	325	335	345	355	365	375	385	395

The chemical reaction is

$$SO_2Cl_2 \rightarrow SO_2 + Cl_2$$

whence

$$C_A = \frac{N}{V} = \frac{p_0 - (p - p_0)}{RT} = \frac{2p_0 - p}{RT}$$

If the reaction is irreversible and of the first order, then

$$-\frac{dC}{d\theta} = k_1 C$$

or

$$\frac{1}{RT}\frac{dp}{d\theta} = \frac{k_1}{RT}(2p_0 - p)$$

and

$$\ln \frac{p_0}{2p_0 - p} = k_1\theta \tag{94}$$

Extrapolation of the original data to $\theta = 0$ indicates p_0 to be 322 mm. The following table shows the values of k_1 calculated from (94):

TABLE III

θ (min.)	p (mm.)	k_1 (sec.$^{-1}$)	k_2 (l/g. mols sec.)
3.4	325	4.6×10^{-5}	0.0050
15.7	335	4.5	0.0051
28.1	345	4.3	0.0049
41.1	355	4.3	0.0050
54.5	365	4.4	0.0050
68.3	375	4.4	0.0052
82.4	385	4.4	0.0053
96.3	395	4.4	0.0054

* *J. Am. Chem. Soc.*, **47**, 1862 (1925).

The value of k_1 is quite constant except for the high value at the first point, which is subject to the greatest experimental error.

If the reaction were second order, the rate equation would be

$$-\frac{dC}{d\theta} = k_2 C^2$$

and on substitution of the value of C and on integration,

$$\frac{1}{2p_0 - p} - \frac{1}{p_0} = \frac{k_2}{RT}\theta \tag{95}$$

The values of k_2 calculated from the data by this equation are tabulated in the preceding table, where numerical values for R and T have been substituted. Although the values of k_2 are very

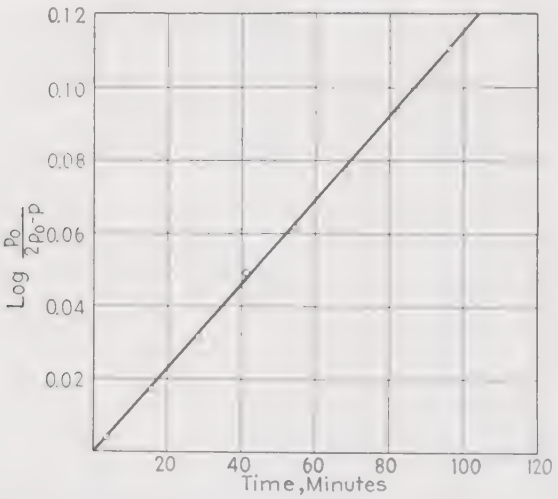

FIG. 27.—Dissociation of sulfuryl chloride (test of first-order reaction).

nearly constant, there is an indication of a definite trend, especially in the later values in the table, which are subject to the least error in calculation.

The corresponding graphical analysis is shown in Figs. 27 and 28. The first shows $\log [p_0/(2p_0 - p)]$ plotted vs. θ, as indicated by (94). Figure 28 shows $1/(2p_0 - p)$ plotted vs. θ, which from (95) should give a straight line if the reaction is second order. It is evident that the data fall on a better straight line on Fig. 27 than on Fig. 28, where a straight line is drawn for comparison. The conclusion is the same as was arrived at by a study of the rate constants, *viz.*, that the data are compatible with the hypothesis of a first-order reaction.

As an example of a more complex reaction, we may employ the data of Patrick and Latshaw* to test the applicability of the third-order rate equation to the oxidation of NO. Known volumes of oxygen and nitric oxide were brought together in a

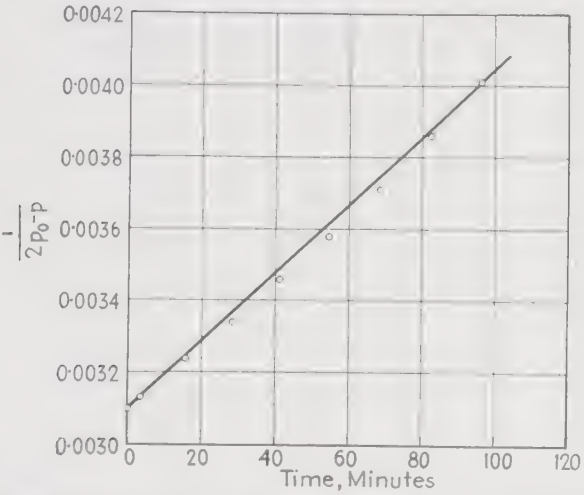

FIG. 28.—Dissociation of sulfuryl chloride (test of second-order reaction.)

reaction vessel, and decrease in total pressure with time measured at constant volume. The following data were obtained at 0°C.:

Time (sec.)		15	20	25	30	45	60
Decrease in total pressure (mm.)		170.1	206.3	227.9	244.3	271.9	287.2
Time (sec.)	75	90	105	120	135	150	165
Decrease in total pressure (mm.)	298.0	306.2	312.9	317.2	320.3	322.7	325.3

The initial pressures of oxygen and nitric oxide were 433.5 and 420.8 mm., respectively. All pressures are given in millimeters of bromonaphthalene, which has a specific gravity of 1.54.

Although the reaction is not reversible, a complication arises because the nitrogen peroxide formed polymerizes instantaneously to form the tetroxide. The equilibrium between these last forms is given by

$$K = \frac{p_{N_2O_4}}{(p_{NO_2})^2} = 51.3 \text{ atm.}^{-1} \text{ at } 0°\text{C.}$$

* *Trans. Am. Inst. Chem. Eng.*, **15**, 221 (1923).

If the pressures are expressed in millimeters of bromonaphthalene, K becomes 0.0076.

The chemical equation is written

$$2NO + O_2 = 2NO_2 \rightleftarrows N_2O_4$$

Since the reaction is at constant volume, the rate equation is

$$\frac{dC_A}{d\theta} = -kC_A^2C_B$$

where C_A is the concentration of NO and C_B is the concentration of oxygen. The gas laws being assumed,

$$C = \frac{N}{V} = \frac{p}{RT}$$

whence

$$\frac{dp_A}{d\theta} = -k\frac{p_A^2p_B}{R^2T^2} = -k_1p_A^2p_B \tag{96}$$

where p_A and p_B are the partial pressures of NO and oxygen, respectively.

Let x represent the mols of oxygen that have disappeared at any time θ, y the mols of NO_2 present, and z the mols of N_2O_4 present. Then

$$2xNO + xO_2 = yNO_2 + zN_2O_4 = yNO_2 + K'y^2N_2O_4$$

where $K' = KRT/V$.

By a nitrogen balance, it follows that

$$2x = y + 2K'y^2$$

When the quadratic for y is solved in terms of x,

$$y = \frac{\sqrt{1 + 16K'x} - 1}{4K'}$$

Since the analysis of the reaction does not depend on the scale of the experiment, we may take any quantity of the initial mixture as a basis. A convenient basis is P_0 mols of oxygen-nitric oxide mixture, where P_0 is numerically equal to the initial pressure expressed in millimeters of bromonaphthalene. With this as a basis $RT = V$, and $K' = K$. Let P represent the total pressure at any time θ. The decrease in total mols is then $P_0 - P$ and may also be expressed in terms of x and y.

$$P_0 - P = (2 + 1)x - y - Ky^2$$
$$= 3x - \frac{\sqrt{1 + 16Kx} - 1}{4K} - \frac{2 + 16Kx - 2\sqrt{1 + 16Kx}}{16K}$$
$$= 2x + \frac{1 - \sqrt{1 + 16Kx}}{8K} \tag{97}$$

The partial pressure of NO and oxygen may now be obtained for substitution in the rate equation, since x may be calculated from (97) if the experimental values of $P_0 - P$ are used. Because of the basis chosen, $p_A = 420.8 - 2x$, and $p_B = 433.5 - x$. These values are given in the following table:

TABLE IV

θ (sec.)	$P_0 - P$	x	p_A	p_B	$\int_{\theta=15}^{\theta=\theta} \frac{dp_A}{p_A^2 p_B} \times 10^8$
15	170.1	108	205	325	0
20	206.3	128	165	305	390
25	227.9	141	139	292	770
30	244.3	150	121	283	1,150
45	271.9	166	89	267	2,280
60	287.2	174	73	259	3,240
75	298.0	180	61	253	4,310
90	306.2	185	51	248	5,610
105	312.9	189	43	244	7,110
120	317.2	191	39	242	8,100
135	320.3	193	35	240	9,330
150	322.7	194	33	239	10,000
165	325.3	195	31	238	10,900

On integrating (96) between the limits of $\theta = 15$ and θ, we have

$$-\int_{\theta=15}^{\theta} \frac{dp_A}{p_A^2 p_B} = k_1(\theta - 15) \tag{98}$$

The integral is plotted vs. $(\theta - 15)$ in Fig. 29, and the straight line lends excellent support to the assumption of a third-order reaction. The values of the integral at large values of θ are the least certain, since p_A, which appears squared, is small and subject to much larger errors than when θ is small. The slope of the line is k_1, from which the reaction-rate constant may be calculated in any desired pressure units using (98), remembering that the values of p_A and p_B have been in millimeters of bromonaphthalene

35. Description of the Flow in a Differential Section of Apparatus Contacting Two Phases by Counterflow. Combined Use of Differential Heat and Material Balance, Rate Equations, and Equilibrium. In order to illustrate how an involved process occurring under widely varying conditions may, when analyzed

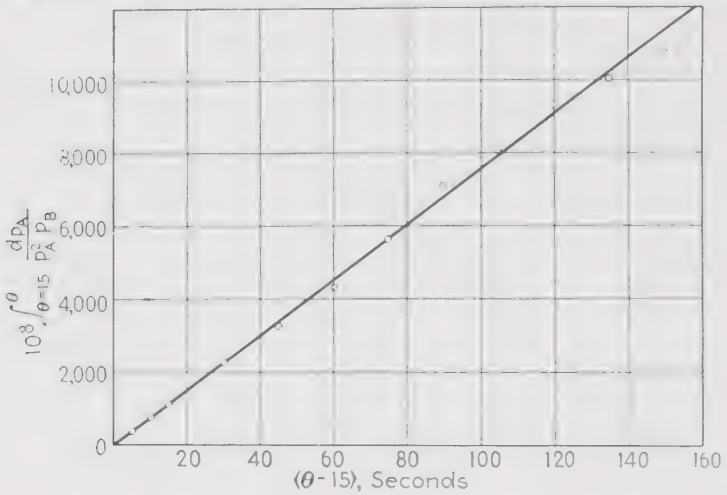

FIG. 29.—Oxidation of NO (test of third-order reaction).

differentially, be broken down into a number of simpler and more fundamental processes occurring simultaneously, we shall consider the countercurrent contacting of a liquid with a gas, there being only one volatile component in the system. This situation might cover such operations as the drying of air by sulfuric acid, the concentration of sulfuric acid by hot flue gases, adiabatic humidification or dehumidification of air, the cooling of water by evaporation into air, various types of absorption and desorption, and a host of other processes too numerous to mention.

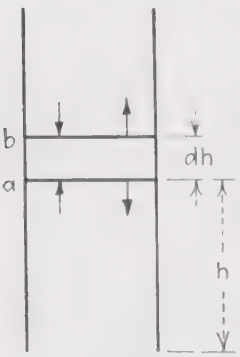

FIG. 30.

Figure 30 illustrates a counterflow tower in which the interaction of the two phases might occur. The carrier gas enters at the bottom and flows up the tower past the liquid, which flows down over suitable packing. The end conditions such as rates of flow, concentrations, temperatures, etc., are assumed constant so that the tower is operating in the steady state and conditions at any point are unchanging with time. Conditions will be assumed constant over any cross section perpen-

dicular to the direction of flow so that all quantities at any point will be completely determined by specification of the distance of this point from either end of the tower. Since conditions may be expected to vary widely throughout the tower, a differential analysis will be necessary, and, in view of the fact that there is but one independent variable involved, it may be anticipated that the description of activity over any differential cross section will be given by ordinary differential equations. Selection of the independent variable as one of the physical properties, or rate of flow of either stream, or position in the tower, is entirely arbitrary and may be made on the basis of convenience. The most convenient independent variable in a case of this kind is usually the position in the tower measured from either end.

As the next step in the analysis, consider the possible processes occurring in a differential section of tower. Since the liquid and gas streams will not in general be in equilibrium with each other, it is possible for both heat and mass transfer to occur (chemical reaction being excluded from the present case), and there exist suitable rate equations describing each of these processes. In general, when mass transfer involving the volatile component occurs, there is a heat effect due to change of state from liquid to gas or vice versa, and we may speak of latent heat being transferred between the two phases. To speak more precisely, within the differential section under consideration there will occur an exchange of enthalpy between the two phases due to transfer of the diffusing substance. On the other hand, if we consider the differential section as a whole and neglect heat losses to the surroundings, the first law of thermodynamics imposes the condition that the total enthalpy input must equal the total enthalpy output so that there must be an enthalpy balance. A final relation holding over this differential section of tower is the material balance, which, since steady-state conditions obtain, reduces to input − output = 0.

Although analytical expressions for each of the relations just mentioned could be presented in such general form as to be applicable to any of the countercurrent processes mentioned above, the technique of formulating the actual equations will be clearer if we consider a definite case—the direct countercurrent contacting of air and liquid water. In developing the differential equations applicable to this case, it must make no difference

whether the apparatus as a whole is an adiabatic humidifier, a dehumidifier, or a water cooler– the equations must be general enough to include all three cases.

In the following derivation, the quantity of water vapor associated with a given amount of air will be expressed in terms of absolute humidity H (lb. water vapor per lb. bone-dry air). The liquid water rate at any cross section will be L lb. water per sq. ft. per hr., and the air rate will be W lb. bone-dry air per sq. ft. per hr. On the basis of 1 sq. ft. of cross section of tower of differential height dh, a water balance may be written involving the usual terms.

Input of water as vapor with air across section $a = WH$
Output of water as liquid across section $a = L$
Input of water as liquid across section $b = L + dL$
Output of water as vapor with air across section b

$$= W(H + dH)$$

Accumulation in section $= 0$
The material balance then becomes

$$WH + (L + dL) - L - W(H + dH) = 0 \tag{99}$$

$$dL = W\,dH \tag{100}$$

It is particularly important to understand the formulation of this equation. A common error consists in placing L equal to the input of liquid water and WH equal to the input of water as vapor, the fact being overlooked that L and WH are in this case at two different cross sections a and b. The output of liquid water is then said to be $L + dL$ and the output of water vapor $W(H + dH)$. Substitution into the material balance then gives

$$L + WH - (L + dL) - W(H + dH) = 0$$

$$dL = -W\,dH \tag{101}$$

where the signs are just reversed from (100). All such difficulties can be avoided if the rule is followed that when a value is assigned to one of the variables corresponding values of the other variables must refer to the same point. Thus, when we say that the input of water as vapor with air across section a is WH, the output of liquid water at this section should be L and not $L + dL$, which should be reserved for the incremental value in L at section b corresponding to $W(H + dH)$.

An alternative method of formulating this differential water balance is to write a finite water balance from the bottom (or the top of the tower) to section a. If subscript 1 designates conditions at the bottom of the tower, this water balance is

$$(L + WH_1) - (L_1 + WH) = 0 \tag{102}$$

Differentiation of (102) results in

$$dL - W\,dH = 0$$

which is identical with (100).

Differential Enthalpy Balance. The base temperature for calculation of enthalpies may be taken arbitrarily as T_0. Liquid water and dry air will be assigned zero enthalpy at T_0. T and t will refer to the temperature of the water and air streams, respectively, at any cross section. C_A and C_S will represent the constant pressure heat capacity per pound of air and water vapor, respectively, and will be assumed constant over the relatively small temperature ranges involved. The enthalpy of 1 lb. of liquid water at temperature T is (considering the heat capacity of liquid water as 1 B.t.u. per lb.) $(1)(T - T_0)$. If h_{fg} is the enthalpy of vaporization of water at the base temperature T_0, the enthalpy per pound of water vapor at t may, as a good approximation over the small temperature range involved, be taken as $h_{fg} + C_S(t - T_0)$. The enthalpy per pound of air is $C_A(t - T_0)$.

We may now tabulate the enthalpy input and output to the differential section. If 1 sq. ft. of cross section is considered,

Enthalpy input by means of air and its associated water vapor across section $a = WHh_{fg} + W(C_A + HC_S)(t - T_0)$

Enthalpy output by means of liquid water across section $a = L(T - T_0)$

Enthalpy output by means of air and its associated water vapor across section b

$= W(H + dH)h_{fg} + W[C_A + (H + dH)C_S](t + dt - T_0)$

Enthalpy input by means of liquid water across section $b = (L + dL)(T + dT - T_0)$.

Equating enthalpy input to enthalpy output and collecting terms give

$$L\,dT = h_{fg}W\,dH + W(C_A + HC_S)dt + WC_S dH(t + dt - T_0) - dL(T + dT - T_0) \tag{103}$$

The term $C_A + HC_s$ represents the heat capacity of 1 lb. of air plus its associated water vapor and is known as the "humid heat" S. The terms $WC_s dH\,dT$ and $dL\,dT$ are differentials of the second order and are negligible compared with the rest of the terms. We now have

$$L\,dT = h_{fg}W\,dH + WS\,dt + WC_s dH(t - T_0) - dL(T - T_0) \tag{104}$$

Before proceeding further with an equation involving several terms, it is always wise to see whether or not any of the terms are possibly negligible compared to others, and if any of the variables change so slightly as to be considered constant. In the case of (104), the variation in the humidity H, through the tower is such that S may be considered constant at an average value, and the term $WC_s dH(t - T_0)$ will be negligible compared with $h_{fg}WdH$. In case the water rate may be taken as constant, the last term on the right also drops out.

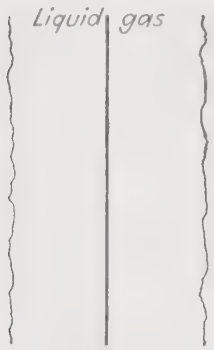

FIG. 31.

Rate Equations. Before formulating the rate equations for heat and mass transfer, let us consider an enlarged section of the interface. According to the film theory, there exists on the gas side of the interface a thin, relatively stagnant film of gas, which merges gradually through an eddy layer into the main turbulent body of gas. A similar picture applies to the liquid side of the interface. In the present case, heat may be transferred from or to the interface and to or from the main body of each stream. Since the interfacial area is unknown in a packed tower, we let a represent the square feet of interfacial area per cubic foot of tower volume and h_g the heat-transfer coefficient of the gas film. The heat transferred per hour across the gas film in the differential volume of tower corresponding to height dh is then $h_g a(T_i - t)dV$ and this must equal the change in sensible heat of the gas stream in passing through this differential section. That is,

$$h_g a(T_i - t)dV = WS\,dt \tag{105}$$

if the basis is 1 sq. ft. of cross section, then $dV = dh$.

Particular attention should be given to the question of signs in this type of equation. Correct signs will always be obtained by

the following method: arbitrarily assume that heat is being transferred in a given direction, let us say from the interface to the main body of the gas. This assumption means that T_i must be greater than t so that $h_g a(T_i - t)$ must be positive. If heat is being transferred to the main body of the gas, as the gas passes up the tower (h increasing) its temperature must increase so that the derivative dt/dh must be positive, and $WS(dt/dh)$, a positive quantity, is equal to $h_g a(T_i - t)$, another positive quantity. If heat were really being transferred in the opposite direction over this differential section $(T_i - t)$ would be negative; and since the gas passing up the tower is now losing heat its temperature t is decreasing as h increases, so that the derivative dt/dh will also be negative. A rate equation of this nature will always have correct signs if the sign of the driving force is consistent with the sign of the derivative involved.

An analogous heat-transfer equation holds on the liquid side of the interface

$$h_l a(T_i - T)dh = -L\,dT \tag{106}$$

but in applying the preceding rule to obtain the correct signs, it must be remembered that liquid is flowing down the tower. If it is assumed arbitrarily that at cross section a heat is being transferred to the main body from the interface, the driving force $(T_i - T)$ will be positive but the derivative dT/dh will be negative, because as we pass to lower cross sections of the tower corresponding to smaller values of h the water temperature T, increases. If Eq. (106) is to be consistent, both sides must be of the same sign and a minus sign must be inserted before the right-hand side. As written, it is capable of providing an accurate description of heat flow either to or from the interface.

The final differential equation is one describing the rate of mass transfer. In the present instance, mass transfer occurs only through the gas film, no concentration gradients being possible in a liquid phase consisting of pure water.

The rate of mass transfer across the gas film is proportional to the difference in partial pressure of water vapor at the interface and in the main body of the gas, and, over reasonably small ranges, partial pressures may be assumed proportional to humidities. As in the case of heat transfer, the coefficient is expressed on the volumetric basis. This gives, on the basis of 1 sq. ft. of tower cross section,

$$k'a(H_i - H)dh = W\,dH \tag{107}$$

The method of determining signs in this equation is analogous to that employed for the heat-transfer equations. When $H_i - H$ is positive, indicating transfer of water vapor to the main body of the gas as it passes up the tower, H necessarily increases with increase in h so that dH/dh is positive and (107) is consistent as written.

We are now in possession of five differential equations containing the seven variables H, H_i, T, T_i, t, L, and h. The necessity for at least one more equation becoming evident, we obtain a relation between H_i and T_i by assuming equilibrium of gas and liquid phases at the interface. From vapor-pressure tables, we immediately obtain p_i at T_i and

$$H_i = \frac{18p_i}{(P - p_i)29} \tag{108}$$

where P is the total pressure.

As there are now five simultaneous differential equations involving essentially six variables, it is possible to determine an integral relationship among these variables. It is shown in Chap. III that the solution of a set of n simultaneous differential equations containing n dependent variables and one independent variable may be made to depend on the solution of an ordinary differential equation of the nth order in two variables. Since the general solution of this nth-order equation must involve n arbitrary constants, the general solution of the present set of five equations will involve five arbitrary constants, the values of which may be determined in terms of the end conditions of the various streams. The statement of these end conditions will reduce the general problem of the interaction of air and water to the particular case of an adiabatic humidifier, dehumidifier, or water cooler.

With the derivation and significance of the preceding equations firmly in mind, it will be of interest to consider briefly a similar problem of very general nature that arises constantly in chemical engineering and applied chemistry. Two or more phases containing several components are to be contacted with each other in a suitable apparatus. Each component may be considered transferable to the other phases with attendant heat effects, and

chemical reactions may occur with liberation or absorption of heat. Given the initial conditions, it is required to determine either the state of the system after a given time of contact or the time of contact required for a given state to be reached. This general problem might include any operation from multicomponent rectification to the catalytic oxidation of ammonia with subsequent oxidation and absorption of the nitrogen oxides. To describe this system, we consider a differential section of the apparatus in which the contact is occurring and apply the usual four types of relationships:

1. *Material Balances.* There will be a differential material balance applying to each component. If chemical reactions are occurring, corresponding stoichiometric relations will be available for use.

2 *First Law of Thermodynamics.* A differential form of the first law may be applied to the section as a whole. If no heat is flowing to or from the surroundings and no work is being done by the system, the first law may reduce to an enthalpy balance which, however, may be complicated by heat effects associated with the various changes of state occurring in the section.

3. *Rate Equations.* Rate equations apply to the transfer of heat across all fluid films, to the mass transfer of each individual component across the films, and to each of the individual chemical reactions occurring in the various films.

4. *Equilibriums.* All available evidence indicates that equilibrium prevails in the region of the interfacial boundary between phases. These equilibriums are constantly shifting until the phases as a whole reach final equilibrium.

It may be observed that a very large number of simultaneous differential equations are required to supply an exact description of many processes, so many, in fact, that they become impractical of manipulation. Consequently, mathematical simplification must be introduced in the form of reasonable simplifying assumptions, and the practical success of such a procedure will depend entirely upon the validity of the simplifying assumptions as revealed by preliminary knowledge or calculation.

Following this procedure, it will be seen that the air-water interaction process may be considerably simplified. The quantity of water passing through the tower is usually quite large compared with the amount of water transferred between

phases so that L may be considered constant through the tower. A second simplification will result when, as is often the case, the liquid film coefficient is so high that temperature gradient across the liquid film is negligible and $T_i = T$. This eliminates the use of the heat-transfer equation for the liquid film and the general solution may be obtained by integration of the three simultaneous differential equations

$$L\,dT = h_{fg}W\,dH + WS\,dt \tag{109}$$

$$Ua(T - t)dh = WS\,dt \tag{110}$$

$$Ka(H_W - H)dh = W\,dH \tag{111}$$

To distinguish equations (110) and (111) from (106) and (107), U and K are employed as over-all coefficients and T and H_W refer to conditions in the main body of the liquid. H_W is the saturation humidity of air in contact with water at temperature T. These equations will be solved in Chap. III as an example of the use of the Milne numerical method of solution of simultaneous differential equations.

CHAPTER III

SOLUTION OF ORDINARY DIFFERENTIAL EQUATIONS

36. Classification. Ordinary differential equations arise generally from a description of situations involving but one independent variable. The most important cases in practice involve, in addition to the independent variable, one dependent variable,* and the most general differential equation in two variables may be written

$$f\left(x,y,\frac{dy}{dx},\frac{d^2y}{dx^2},\frac{d^3y}{dx^3}\cdots\frac{d^ny}{dx^n}\right)=0 \tag{1}$$

Any value of y, which when substituted into (1) reduces the left-hand side to zero, is called a "solution" of the differential equation. As pointed out in Par. 16, a differential equation containing a derivative of the nth order can be derived from an equation between x and y involving n independent arbitrary constants by n successive differentiations of the equation. The resulting n equations together with the original equation constitute a set of $n+1$ equations from which the n constants can be eliminated to obtain (1). This process of obtaining a differential equation from its primitive is comparatively easy to perform.

Conversely, it is shown in treatises on differential equations that any equation of the type of (1) possesses a solution and that the most general form of this solution is a relationship between x, y, and n arbitrary constants, *i.e.*,

$$F(x,y,c_1,c_2,c_3\cdots c_n)=0 \tag{2}$$

If (2) is solved for y and substituted in (1), it must reduce the left-hand side of the latter to zero. From a practical stand-

* The differentiation of functions of three or more variables gives rise to two types of differential equations. The first type contains one independent variable and several dependent variables. An example is the differential enthalpy balance [Eq. (103), Par. 35, Chap. II]. These are ordinary differential equations. The second type contains two or more independent variables. These contain partial derivatives and are called "partial differential equations."

point, it may not help a great deal to know that (1) has a solution, for experience has shown that the problem of obtaining this solution is frequently difficult, solutions having been obtained for only comparatively few of the many possible types of equations. Furthermore, the fact that a solution exists does not imply that this solution is expressible in the form of elementary functions. Such an innocent-looking equation as

$$\frac{dy}{dx} = x^2 + y^2$$

has no solution in the form of known functions. It is fortunate that many important physical problems of common occurrence give rise to equations that have been solved.

In the present chapter, the most important equations of common occurrence will be listed and their solutions indicated, and an attempt will be made to indicate the types of equations that can and that cannot be solved by elementary methods.

The equations that have proved most amenable to solution are those involving the dependent variable and its derivatives to the first power only. These are known as "linear differential equations."

Although very few nonlinear equations have been solved, there are several standard forms that occur repeatedly and admit of ready solution. The majority of these are equations of the first order and first degree, and their nonlinear character arises from the dependent variable being present to other powers than the first.

EQUATIONS OF THE FIRST ORDER

Any differential equation of the first order and first degree in dy/dx may be written in the form

$$M\,dx + N\,dy = 0 \tag{3}$$

where M and N are functions of x and y. Several classes of equations of this form are easily solved.

37. Separable Equations. If (3) can be reduced to the form

$$f_1(x)dx + f_2(y)dy = 0 \tag{4}$$

the variables are said to be "separated," and the solution is

$$\int f_1(x)dx + \int f_2(y)dy = C \tag{5}$$

The two constants accompanying the two indefinite integrals on the left are not independent but may be combined as the single constant C.

Very frequently the possibility of separation of the variables may not be immediately evident but may be feasible with sufficient ingenuity. Consider the equation

$$x(1 + y^2)^{\frac{1}{2}} + y(1 + x^2)^{\frac{1}{2}}\frac{dy}{dx} = 0 \tag{6}$$

After being written in the form

$$x(1 + y^2)^{\frac{1}{2}}dx = -y(1 + x^2)^{\frac{1}{2}}dy$$

the equation is seen to be separable and is easily transformed to the standard form

$$\frac{x\,dx}{(1 + x^2)^{\frac{1}{2}}} + \frac{y\,dy}{(1 + y^2)^{\frac{1}{2}}} = 0$$

the integral of which is

$$(1 + x^2)^{\frac{1}{2}} + (1 + y^2)^{\frac{1}{2}} = C$$

38. Equations Made Separable by Change of Variable. In some cases, separation of the variables may be effected by a suitable change of variable. For example, the equation

$$(xy^2 + y)dx - x\,dy = 0 \tag{7}$$

may be made separable by placing $xy = v$; then $dv = x\,dy + y\,dx$, and substitution gives

$$\left(\frac{v^2}{x} + \frac{v}{x}\right)dx + \frac{v\,dx}{x} - dv = 0$$

$$\frac{dx}{x} - \frac{dv}{v(v + 2)} = 0$$

$$\ln x + \frac{1}{2}\ln\frac{v + 2}{v} = C_1$$

$$x\left(\frac{v + 2}{v}\right)^{\frac{1}{2}} = e^{C_1}$$

$$x^2\left(1 + \frac{2}{xy}\right) = e^{2C_1} = C$$

This example illustrates the point that a solution may be written in several different equivalent forms.

No general rule for reduction of an equation to simpler form by substitution and change of variable may be given. Often some of the quantities that occur in the statement of the problem may suggest themselves as good variables, and often some expression in the differential equation will indicate a simplifying substitution. For example, if y enters the equation only as y^2 and $y(dy/dx)$, we may take $y^2 = u$, whereupon

$$y(dy/dx) = \tfrac{1}{2}(du/dx),$$

and a simplification has been effected.

39. Homogeneous Equations. Any function $f(x,y)$ is said to be a "homogeneous function" of the nth degree, if when x and y are multiplied by t, the function is multiplied by t^n. Thus if the function f is homogeneous in x and y,

$$f(tx,ty) = t^n f(x,y) \tag{8}$$

If the coefficients M and N in (3) are homogeneous and of the same degree in x and y, it is easily shown that the substitution $y = ux$ will make the equation separable. Equation (3) may be written

$$f_1(x,y)dx + f_2(x,y)dy = 0 \tag{9}$$

If ux is substituted for y, the result is to multiply each term of $f_1(1,u)$ and $f_2(1,u)$ by x; and since f_1 and f_2 are assumed to be homogeneous and of the same degree, (9) may be written

$$x^n f_1(1,u)dx + x^n f_2(1,u)(u\,dx + x\,du) = 0$$

After separation of the variables, the equation becomes

$$\frac{dx}{x} + \frac{f_2(1,u)du}{f_1(1,u) + uf_2(1,u)} = 0$$

the solution of which is

$$\ln x + \int \frac{f_2(1,u)du}{f_1(1,u) + uf_2(1,u)} = C \tag{10}$$

As an example of the use of this method, consider the homogeneous equation of the second degree

$$y^2\,dx + (x^2 - xy)dy = 0 \tag{11}$$

The substitution $y = ux$ could be made directly, but it is convenient to use the formula just derived.

$$f_1(x,y) = y^2; \qquad f_1(1,u) = u^2.$$
$$f_2(x,y) = (x^2 - xy); \qquad f_2(1,u) = (1 - u)$$
$$\int \frac{(1-u)du}{u^2 + u - u^2} = \int \frac{du}{u} - \int du = \ln u - u = \ln \frac{y}{x} - \frac{y}{x}$$

The solution according to (10) is now written

$$\ln x + \ln \frac{y}{x} - \frac{y}{x} = c \tag{12}$$

Equivalent forms are

$$\ln y = c + \frac{y}{x} \tag{13}$$

$$y = e^{\left(c + \frac{y}{x}\right)} = e^c \cdot e^{\frac{y}{x}} = C_1 e^{\frac{y}{x}} \tag{14}$$

After a differential equation has been solved, it is always wise to check the solution by differentiation. Differentiation of (13) gives

$$\frac{dy}{y} = \frac{x\,dy - y\,dx}{x^2}$$

Clearing of fractions gives (11).

40. Equations of First Order and First Degree with Linear Coefficients. In the equation

$$(ax + by + c)dx + (gx + hy + k)dy = 0 \tag{15}$$

the coefficients of dx and dy are linear in x and y. Such an equation can usually be made homogeneous by the substitutions

$$\left.\begin{aligned} x &= w + m; & dx &= dw \\ y &= v + n; & dy &= dv \end{aligned}\right\} \tag{16}$$

the constants m and n being evaluated to satisfy the equations

$$\left.\begin{aligned} am + bn + c &= 0 \\ gm + hn + k &= 0 \end{aligned}\right\} \tag{17}$$

If $a/g = b/h$, Eq. (17) will be inconsistent. In this case, elimination of y in (15) by the substitution $w = ax + by$ will provide a separable equation in x and w.

As an example, this method will be applied to the equation

$$(x + 3y + 4)dx + (2x + y + 3)dy = 0 \tag{18}$$

Equations (17) become

$$m + 3n + 4 = 0$$
$$2m + n + 3 = 0$$

whence

$$n = m = -1$$

and

$$(w - 1 + 3v - 3 + 4)dw + (2w - 2 + v - 1 + 3)dv = 0$$
$$(w + 3v)dw + (2w + v)dv = 0 \tag{19}$$

This is a homogeneous equation in w and v, and the method of Par. 39 is applicable.

Let $v = uw$, and solve without the formula.

$$dv = u\,dw + w\,du$$
$$(w + 3uw)dw + (2w + uw)(u\,dw + w\,du) = 0$$

Division through by w and separation of the variables result in

$$\frac{dw}{w} + \frac{(2 + u)du}{1 + 5u + u^2} = 0$$

Integration gives

$$\ln w - \frac{1}{2\sqrt{21}} \ln \frac{2u + 5 - \sqrt{21}}{2u + 5 + \sqrt{21}} + \frac{1}{2} \ln (1 + 5u + u^2) = C_1$$

Substitution of $w = x + 1$ and $u = (y + 1)/(x + 1)$ gives the required solution, which may be expressed in several different forms by algebraic rearrangements.

41. Exact Equations. The complete significance and precise definition of an exact differential will be developed more fully in Chap. IV, and the present discussion will be limited to those properties of importance for the solution of first-order equations. Consider the function

$$3x^2y^2 + 2y^3x + y^2 + C = 0 \tag{20}$$

Differentiating gives

$$6y^2x\,dx + 6x^2y\,dy + 2y^3dx + 6y^2x\,dy + 2y\,dy = 0 \tag{21}$$

The quantity on the left of (21) is called an "exact differential" of the function (20), because it is the result of differentiation only, no other algebraic operations having been performed. Consequently, by one integration of (21), it is possible to obtain (20).

When (21) is written in the standard form (3),

$$(6y^2x + 2y^3)dx + (6x^2y + 6y^2x + 2y)dy = 0 \qquad (22)$$

Considering x constant, differentiate M, the coefficient of dx, with respect to y; *i.e.*, obtain the partial derivative of M with respect to y.

$$\frac{\partial M}{\partial y} = 12xy + 6y^2$$

Obtain next the partial derivative of N, the coefficient of dy, with respect to x.

$$\frac{\partial N}{\partial x} = 12xy + 6y^2$$

Obviously $\partial M/\partial y = \partial N/\partial x$ and, as shown in Chap. IV, this is the necessary and sufficient condition that any function $(M\,dx + N\,dy)$ be an exact differential.

Returning now to (22), divide through by $2y$, obtaining

$$(3yx + y^2)dx + (3x^2 + 3yx + 1)dy = 0 \qquad (23)$$

or

$$M_1dx + N_1dy = 0$$

After this division,

$$\frac{\partial M_1}{\partial y} = 3x + 2y; \qquad \frac{\partial N_1}{\partial x} = 6x + 3y$$

and since the two partial derivatives are no longer equal, (23) is no longer an exact differential and cannot be integrated directly to give its primitive (20). Assuming that we were to start with the differential Eq. (23), we could render it directly integrable, *i.e.*, we could make it an exact differential by multiplying through by the factor $2y$ previously canceled. Such a factor is called an "integrating factor," and it may be shown that for any equation of the form of (3) an infinite number of integrating factors exist. Although no general method is known for finding integrating factors, they are known in a few cases. The most important of these is the linear differential equation of the first order.

42. Linear Equation of the First Order. The most general form of this equation may be written

$$\frac{dy}{dx} + Py = Q \qquad (24)$$

where P and Q are constants or functions of x only. If (24) is multiplied by the integrating factor $e^{\int P\,dx}$, it becomes

$$e^{\int P\,dx}\frac{dy}{dx} + e^{\int P\,dx}Py = e^{\int P\,dx}Q \tag{25}$$

The left-hand side is clearly the derivative of the quantity $ye^{\int P\,dx}$, so that the equation is exact and its solution is

$$ye^{\int P\,dx} = \int e^{\int P\,dx}Q\,dx + C \tag{26}$$

43. Equations Reducible to Linear Form. Bernoulli's Equation. Differential equations can occur in so many different forms that the ability to effect simplification and reduction to a standard form by judicious substitutions and change of variable is of paramount importance for success in solution. An example of a successful substitution, not at all obvious, is provided by the equation

$$x\,dy + (y - y^2 \ln x)dx = 0 \tag{27}$$

Place $\ln x = v$, then $x = e^v$ and $dx = e^v \cdot dv$. Substituting in (27) gives

$$e^v dy + y(1 - yv)e^v dv = 0 \tag{28}$$

Dividing through by $e^v dv$ gives

$$\frac{dy}{dv} + y = vy^2 \tag{29}$$

(29) is a special case of Bernoulli's equation, which may be written

$$\frac{dy}{dx} + Py = Qy^n \tag{30}$$

where P and Q are again constants or functions of x. This equation may be made linear upon division by y^n and substitution of $y^{1-n} = z$. Applying this to (29), we have

$$\frac{1}{y^2}\frac{dy}{dv} + \frac{1}{y} = v \tag{31}$$

Placing $y^{1-2} = \frac{1}{y} = z$ we have $\frac{dy}{dv} = -\frac{1}{z^2}\frac{dz}{dv}$

Substituting in (31) gives the linear equation

$$\frac{dz}{dv} - z = -v \tag{32}$$

The integrating factor is $e^{\int -dv} = e^{-v}$ and the solution is

$$ze^{-v} = \int -ve^{-v}dv + c$$

Integrating by parts results in

$$ze^{-v} = ve^{-v} + e^{-v} + c \tag{33}$$

When z and v are replaced by their values in terms of x and y,

$$\frac{1}{y}e^{-\ln x} = e^{-\ln x} \ln x + e^{-\ln x} + c \tag{34}$$

but $e^{-\ln x} = 1\ x$ by definition of $\ln x$, so that the final solution may be written

$$\frac{1}{y} = \ln x + 1 + cx$$

44. Other Integrating Factors. The following special cases are often mentioned with reference to (3):

If $[(\partial M/\partial y) - (\partial N/\partial x)]/N = f(x)$, then $e^{\int f(x)dx}$ is an integrating factor.

If $[(\partial M/\partial y) - (\partial N/\partial x)]/M = f(y)$, then $e^{-\int f(y)dy}$ is an integrating factor.

If $M = yf_1(x,y)$, and $N = xf_2(x,y)$, then $1/(xM - yN)$ is an integrating factor.

In practice, unless the equation falls under one of the standard forms, the determination of an integrating factor is difficult and no attempt should be made to find one until other methods of integration have failed.

45. Integration of Exact Equations. When the integral of an exact equation is not obvious upon inspection, the following procedure is recommended. It is shown in Chap. IV that when $f(x,y) = 0$ is differentiated

$$df(x,y) = \frac{\partial f(x,y)}{\partial x}dx + \frac{\partial f(x,y)}{\partial y}dy = M\,dx + N\,dy \tag{35}$$

Operating in this manner upon (20), where

$$f(x,y) = 0 = 3x^2y^2 + 2y^3x + y^2 + C \tag{20}$$
$$\frac{\partial f(x,y)}{\partial x} = 6y^2x + 2y^3$$
$$\frac{\partial f(x,y)}{\partial y} = 6x^2y + 6xy^2 + 2y$$

and

$$df(x,y) = 0 = (6y^2x + 2y^3)dx + (6x^2y + 6y^2x + 2y)dy \tag{22}$$

yields the result obtained previously by ordinary differentiation.

If the coefficient of dx, M, is integrated with respect to x, y being treated as a constant, we obtain

$$\int M\,dx = \int \frac{\partial f(x,y)}{\partial x}dx = 3y^2x^2 + 2y^3x + f_c(y) \tag{36}$$

Since y was held constant during the integration, the constant of integration must be considered a function of y, $f_c(y)$; and to complete the integration, the form of $f_c(y)$ must be determined.

Differentiation of (36) gives

$$(6y^2x + 2y^3)dx + \left[6x^2y + 6y^2x + \frac{df_c(y)}{dy}\right]dy = 0$$

By comparison with the original differential Eq. (22), it is seen that $[df_c(y)]\,dy = 2y$, and integration gives $f_c(y) = y^2 + c$.

The same result may usually be obtained by either of the following rules: (1) Integrate $M\,dx$, considering y constant, and add the integral with respect to y of those terms in N which do not contain x. (2) Integrate $N\,dy$, considering x constant, and add the integral with respect to x of those terms in M which do not contain y.

46. Equations of the First Order and Higher Degree. The general equation of this type is

$$f\left(x,y,\frac{dy}{dx}\right) = 0 \tag{37}$$

CASE I. Equations Solvable for $dy\,dx$. After solving for $dy\,dx$, treat each of the solutions as it occurs under some case mentioned previously. A typical equation of this class is

$$\left(\frac{dy}{dx}\right)^2 + \frac{dy}{dx} - 6 = 0 \tag{38}$$

This is equivalent to

$$\left(\frac{dy}{dx} + 3\right)\left(\frac{dy}{dx} - 2\right) = 0 \tag{39}$$

which has two solutions

$$\frac{dy}{dx} = -3, \qquad \text{from which} \qquad y = -3x + c_1$$

and

$$\frac{dy}{dx} = 2, \qquad \text{from which} \qquad y = 2x + c_2$$

These solutions may be used separately or, if desired, they may be combined by multiplication, which in this case would give

$$(y + 3x - c)(y - 2x - c) = 0 \tag{40}$$

Since y can be determined only by equating one of these factors to 0 and since both constants are arbitrary, it is allowable to use the same symbol c for each.

There is an important difference between first-order equations of the first and higher degrees in dy dx. Whereas an equation of first order and first degree determines one slope at any point x, y, an equation of first order and second degree, having two values of dy/dx, determines two slopes at any point. In general, a first-order equation of degree n in dy/dx will determine n slopes at every point, although these may not all apply to real curves.

The constants c_1 and c_2 arising from the two solutions of (38) are not arbitrary in the sense that the solution can be made to fit two independent initial conditions. Since (38) determines two slopes at every point, the general solution must represent two curves through every point and, hence, the two values of c for every point.

CASE II. Equations Solvable for y. Solution of the general equation for y gives one or more equations of the form

$$y = f_1\left(x, \frac{dy}{dx}\right) \tag{41}$$

Differentiating with respect to x and substituting $dy/dx = p$ result in

$$p = f_2\left(x,p,\frac{dp}{dx}\right) \tag{42}$$

If (42) may be integrated to give

$$f_3(x,p,c) = 0 \tag{43}$$

then p may be eliminated between (41) and (43) to give a relation between x, y, and c, which in general is the solution of (41). Inasmuch as the process of elimination may introduce extraneous factors, the solution should always be checked by differentiation. If desired, the two equations (41) and (43) may be retained as a solution, p being a parameter the value of which determines x and y.

CASE III. Equations Solvable for x. Solution of the general equation for x gives one or more equations of the form

$$x = f_4\left(y,\frac{dy}{dx}\right) \tag{44}$$

Differentiate with respect to y, and substitute $dx/dy = 1/p$, to obtain

$$\frac{1}{p} = f_5\left(y,p,\frac{dp}{dy}\right) \tag{45}$$

If the integral relation between p and y can be obtained from (45), the elimination of p between this integral and (44) will give a solution in terms of x and y. Otherwise, a parametric solution is indicated as in Case II.

An example of an equation that can be solved for either dy/dx, y, or x is

$$x - k\left(\frac{dy}{dx}\right)^2 = y\frac{dy}{dx} \tag{46}$$

In a case like this, there is no guide but experience to indicate which procedure is most satisfactory. As a first trial, let us solve for dy/dx by the quadratic formula

$$\frac{dy}{dx} = \frac{-y \pm \sqrt{y^2 + 4kx}}{2k} \tag{47}$$

Equation (47) does not appear particularly promising of solution by any of the previous methods; so we shall try solving (46) for y, placing $dy/dx = p$. This gives

$$y = \frac{x - kp^2}{p} \tag{48}$$

Differentiating (48) with respect to x in order to eliminate y gives

$$\frac{dy}{dx} = p = \frac{p\left(1 - 2kp\frac{dp}{dx}\right) - (x - kp^2)\frac{dp}{dx}}{p^2} \tag{49}$$

Multiplying each side by p^2 and factoring out dp/dx result in the much simpler form

$$p - p^3 = (x + kp^2)\frac{dp}{dx} \tag{50}$$

If (50) is written in the form

$$\frac{dx}{dp} = \frac{x + kp^2}{p - p^3} \tag{51}$$

it is apparent that the result is a linear equation of the first order in x. This may be integrated by the method of Par. 42 to give a relation between x and p, which with (48) constitutes a solution in the form of a pair of parametric equations in which any value of p determines a value for x and for y.

If the original equation (46) had been solved for x, the solution would turn out to be very similar.

47. Clairaut's Equation. This equation, usually written

$$y = x\left(\frac{dy}{dx}\right) + f\left(\frac{dy}{dx}\right) \tag{52}$$

is an important case of an equation solved for y. Placing $dy/dx = p$ and differentiating with respect to x give

$$p = p + x\frac{dp}{dx} + f'(p)\frac{dp}{dx} \tag{53}$$

Factoring out dp/dx produces

$$[x + f'(p)]\frac{dp}{dx} = 0 \tag{54}$$

In (54), either $dp/dx = 0$, or $x + f'(p) = 0$. If $dp/dx = 0$, $p = c$, and by substitution in (52) the family of lines $y = cx + f(c)$ is a solution.

Another solution may be obtained by eliminating p from (52) and $x + f'(p) = 0$. Although this solution will satisfy the original equation, it obviously contains no arbitrary constant and, hence, cannot be the general solution. This leads us to the consideration of a third type of solution of a differential equation, the singular solution.

48. Singular Solutions. It is instructive to consider the geometric interpretation of a singular solution, and for this purpose it will be convenient to take the special case of Clairaut's equation

$$y = px + 2p \qquad (55)$$

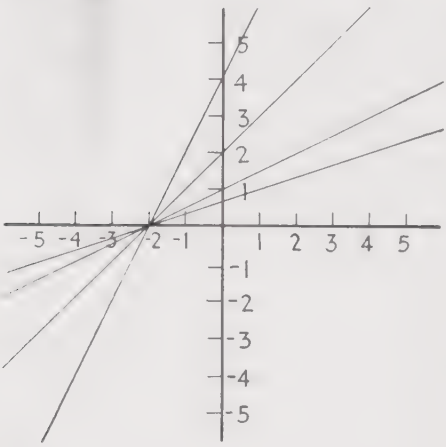

FIG. 32.

Differentiating with respect to x results in

$$\frac{dp}{dx}(x + 2) = 0 \qquad (56)$$

The general solution, containing one arbitrary constant, is

$$y = cx + 2c \qquad (57)$$

The other factor gives $x = -2$, which when substituted into (55) gives $y = 0$. As may be verified by substitution in (55), $y = 0$, $x = -2$ is a solution, and since this solution can in no way be obtained from the general solution (57), regardless of the value assigned to the arbitrary constant, it is called a "singular solution." Equation (57) represents a family of straight lines having y intercepts always twice the corresponding slopes (Fig. 32). The singular solution is the locus of the intersection of this family of lines, which in this case is a single point.

A more common type of singular solution arises from the solution of the equation

$$y = px + p^2 \qquad (58)$$

the general solution of which is

$$y = cx + c^2 \qquad (59)$$

and the singular solution obtained by the preceding method

$$y = -\frac{x^2}{4} \tag{60}$$

Equation (59) represents a family of straight lines, the slopes of which are the square roots of their respective y intercepts. As shown in Fig. 33, these lines are tangent to the parabola $y = -(x^2/4)$, and the parabola is known as the "envelope locus" of the family of lines. Although the envelope locus cannot be obtained from the general solution, every point on

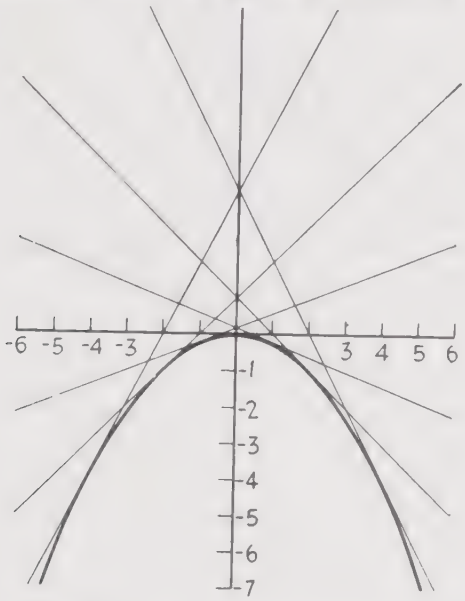

FIG. 33.—Loci of singular solutions.

the envelope locus will also satisfy a particular solution obtained from the general solution by assigning the proper value to c.

Any suspected singular solution should always be checked by insertion in the original equation, for the operations of elimination and substitution may give rise to types of loci that are not solutions.

SPECIAL TYPES OF SECOND-ORDER EQUATIONS

49. Equations with Missing Terms. It is not uncommon to encounter second-order equations that are lacking in either y, x, or both y and x. By proper substitutions, the solution of such an equation may be made to depend upon a first-order equation.

CASE I. Equations Not Containing y. If the equation does not contain dy/dx, it may be written in the form

$$\frac{d^2y}{dx^2} = f(x) \tag{61}$$

and solved directly by two integrations.

If dy/dx is present, the equation can be written in the form

$$\frac{d^2y}{dx^2} = f\left(x, \frac{dy}{dx}\right) \tag{62}$$

The substitution $dy/dx = p$ will reduce (62) to an equation of the first order in p and x. To illustrate, let us solve

$$\frac{d^2y}{dx^2} + x\frac{dy}{dx} = x \tag{63}$$

Let $dy/dx = p$, so that $d^2y/dx^2 = dp/dx$.
After substitution, we have a separable equation

$$\frac{dp}{dx} + px = x \tag{64}$$

$$\frac{dp}{1 - p} = x\,dx \tag{65}$$

The integral of (64) is

$$-\ln(1 - p) = \frac{x^2}{2} + C_1' \tag{66}$$

which may be written in the exponential form

$$p = \frac{dy}{dx} = 1 - C_1 e^{-\frac{x^2}{2}} \tag{67}$$

Integration of (66) gives the final solution (67)

$$y = x - C_1 \int e^{-\frac{x^2}{2}} dx + C_2 \tag{68}$$

The integral in (68) cannot be expressed in terms of a finite number of elementary functions. One method of making the solution assume a useful form would be to expand $e^{-\frac{x^2}{2}}$ in an infinite series and integrate each term of the series, as explained in Chap. V.

CASE II. Equations Not Containing x. Here again, the substitution of $p = dy/dx$ will reduce the equation to one of

the first order. Instead of replacing d^2y/dx^2 by dp/dx as in Case I, we note that

$$\frac{dp}{dx} = \frac{dp}{dy} \cdot \frac{dy}{dx} = p\frac{dp}{dy} \tag{69}$$

As an example of this technique, consider the solution of the equation

$$y\frac{d^2y}{dx^2} = 1 + \left(\frac{dy}{dx}\right)^2 \tag{70}$$

The preceding substitutions reduce this to

$$yp\frac{dp}{dy} = 1 + p^2 \tag{71}$$

in which the variables can be separated to give

$$\frac{p\,dp}{1 + p^2} = \frac{dy}{y} \tag{72}$$

The integral is $\frac{1}{2} \ln (1 + p^2) = \ln y + C_1'$
Solving for p produces

$$p = \pm\sqrt{c_1y^2 - 1} = \frac{dy}{dx} \tag{73}$$

A second integration results in the general solution

$$\pm x = \int \frac{dy}{\sqrt{c_1y^2 - 1}} + c_2 = \frac{1}{\sqrt{c_1}} \ln (y\sqrt{c_1} + \sqrt{c_1y^2 - 1}) + c_2 \tag{74}$$

LINEAR DIFFERENTIAL EQUATIONS

50. General Properties of Linear Equations. The general linear equation of the nth degree may be written

$$\frac{d^ny}{dx^n} + X\frac{d^{n-1}y}{dx^{n-1}} + \cdots X_{n-1}\frac{dy}{dx} + X_ny = Q \tag{75}$$

$X \ldots X_{n-1}$ X_n, and Q are functions of x or constants.

If I is any solution of this equation, the general solution may be represented by

$$y = I + Z \tag{76}$$

where Z is some function of x.
If the value of y given by (76) is substituted in the general equation, the result is

$$\left(\frac{d^nI}{dx^n} + X\frac{d^{n-1}I}{dx^{n-1}} + \cdots X_{n-1}\frac{dI}{dx} + X_nI\right) + \left(\frac{d^nZ}{dx^n} + X\frac{d^{n-1}Z}{dx^n} + \cdots X_{n-1}\frac{d^{n-1}Z}{dx^n} + X_nZ\right) = Q \quad (77)$$

But since I is assumed to be a solution of (75), the first member of (77) is equal to Q, and the second member must equal zero. The equation

$$\frac{d^ny}{dx^n} + X\frac{d^{n-1}y}{dx^n} + \cdots X_{n-1}\frac{d^{n-1}y}{dx^n} + X_ny = 0 \quad (78)$$

is called the "reduced equation," and Z is its general solution. We may now state the first important property.

Property I. The general solution of (75) is the sum of any solution I, called the "particular integral," and Z, called the "complementary function." It is important to note that the equation giving rise to the complementary function is the same as the left-hand side of the original equation placed equal to zero. If, in the original equation, $Q = 0$, it is obvious that the complementary function will constitute the general solution.

Property II. If Y_1 is any particular solution of the reduced Eq. (78), then c_1Y_1 is also a solution and the general solution of the reduced equation is

$$y = c_1Y_1 + c_2Y_2 + \cdots c_nY_n \quad (79)$$

provided that the particular solutions Y_1, $Y_2 \cdots Y_n$ are linearly independent.* That (79) is a solution of (78) may be verified by direct substitution, and it is the general solution since it contains n arbitrary constants.

Property III. If a single solution of the reduced equation is known, the order of this equation may be lowered by unity; and if m solutions of the reduced equation are known, its order may be reduced by m. This simplifying process will be demonstrated on an equation of the second degree.

Assume that Y_1 is known to be a particular solution of the equation

$$\frac{d^2y}{dx^2} + f_1(x)\frac{dy}{dx} + f_2(x)y = 0 \quad (80)$$

* The condition of linear independence means that it is impossible to find a set of constants $c_1, c_2 \ldots c_n$ other than zero, such that for all values of x, $c_1Y_1 + c_2Y_2 + \cdots c_nY_n = 0$.

Place $y = Y_1 z$; then

$$\frac{dy}{dx} = Y_1 \frac{dz}{dx} + z \frac{dY_1}{dx}$$

and

$$\frac{d^2y}{dx^2} = Y_1 \frac{d^2z}{dx^2} + \frac{dz}{dx}\frac{dY_1}{dx} + z\frac{d^2Y_1}{dx^2} + \frac{dY_1}{dx}\frac{dz}{dx}$$

Substituting in (80) and collecting terms produce

$$Y_1 \frac{d^2z}{dx^2} + f_1(x) Y_1 \frac{dz}{dx} + 2\frac{dz}{dx}\left(\frac{dY_1}{dx}\right) + z\left[\left(\frac{d^2Y_1}{dx^2} + f_1(x)\frac{dY_1}{dx} + f_2(x)Y_1\right)\right] = 0 \quad (81)$$

Since Y_1 is a solution of (80), the coefficient of z is zero; and if dz/dx is placed equal to u, (81) becomes

$$Y_1 \frac{du}{dx} + u\left[Y_1 f_1(x) + 2\frac{dY_1}{dx}\right] = 0 \quad (82)$$

As Y_1, being a solution of (80), is a known function of x, (82) is a linear equation of the first order in u. Similar methods of operation are applicable to equations of higher order.

Although the properties that have just been enumerated belong to all linear equations, their use is best demonstrated in the solution of linear equations with constant coefficients, since the general linear equations with variable coefficients must be solved in series.

51. Solution of Linear Equations with Constant Coefficients. The general linear equation with constant coefficients may be written

$$\frac{d^ny}{dx^n} + a_1\frac{d^{n-1}y}{dx^{n-1}} + \cdots a_{n-1}\frac{dy}{dx} + a_n y = Q \quad (83)$$

where the a's are constants and Q may be constant or a function of x.

To solve this equation, it is convenient to introduce the notation of differential operators in which the operation of differentiating y with respect to x is written Dy. The symbol D thus stands for d/dx, and d^ny/dx^n is written D^ny. In this notation, (83) becomes

$$D^ny + a_1D^{n-1}y + \cdots a_{n-1}Dy + a_n y = Q \quad (84)$$

With no ambiguity, (84) may be written

$$(D^n + a_1D^{n-1} + \cdots a_{n-1}D + a_n)y = Q \tag{85}$$

The expression in parenthesis is known as a "linear differential operator of order n" and it may be shown that this operator, which looks like an algebraic polynomial in D, follows the laws of operation associated with polynomials. For example,

$$D(y^2 + y^3) = Dy^2 + Dy^3;\ D \cdot Dy = D^2y;$$
$$(D^2 - 1)y = (D - 1)(D + 1)y = (D + 1)(D - 1)y$$

The validity of these last transformations becomes clear if we carry out the indicated operations

$$(D^2 - 1)y = \frac{d^2y}{dx^2} - y$$

$$(D - 1)(D + 1)y = (D - 1)\left(\frac{dy}{dx} + y\right) = D\left(\frac{dy}{dx} + y\right) - \frac{dy}{dx} - y$$

$$= \frac{d^2y}{dx^2} + \frac{dy}{dx} - \frac{dy}{dx} - y = \frac{d^2y}{dx^2} - y \tag{86}$$

The result is the same irrespective of which factor is taken first

With reference to the general operator in (85), it is clear that it may be considered as an algebraic polynomial of degree n. It is shown in algebra that such a polynomial has n roots r_1, $r_2 \ldots r_n$, so that when the roots are known we may write

$$(D^n + a_1D^{n-1} + \cdots a_{n-1}D + a_n)y = (D - r_1)(D - r_2) \cdots (D - r_n)y$$

Furthermore, the positions with respect to y of the factors on the right may be interchanged with no effect on the result.

The general solution of (83) may now be written as

$$y = \frac{1}{(D - r_1)(D - r_2) \cdots (D - r_n)}(Q) \tag{87}$$

and may be expressed in usable form as soon as we discover the significance of the reciprocal of the operator. In order to do this, consider a linear equation

$$(D - r_1)y = Q$$

The solution of this equation, already given in Par. 42, is

$$y = e^{r_1x}\int e^{-r_1x}Q\,dx + c_1e^{r_1x} \tag{88}$$

Written in operational form, the solution is

$$y = \frac{1}{(D - r_1)}Q \tag{89}$$

Comparison of (88) and (89) shows the significance of $1/(D - r_1)$. Consider next the second-order equation

$$(D - r_2)(D - r_1)y = Q \tag{90}$$

$$(D - r_2)y = \left(\frac{1}{D - r_1}\right)Q = e^{r_1 x}\int e^{-r_1 x}Q\,dx + C_1 e^{r_1 x} \tag{91}$$

$$y = \left(\frac{1}{D - r_2}\right)\left[e^{r_1 x}\int e^{-r_1 x}Q\,dx + C_1 e^{r_1 x}\right] =$$

$$e^{r_2 x}\int e^{-r_2 x}\left[e^{r_1 x}\int e^{-r_1 x}Q\,dx + C_1 e^{r_1 x}\right]dx + C_2 e^{r_2 x} =$$

$$e^{r_2 x}\int e^{(r_1 - r_2)x}\int e^{-r_1 x}Q\,(dx)^2 \tag{92}$$

where it is understood that an additive constant will be inserted after each integration. If these constants are placed equal to zero, a particular solution, *i.e.*, a particular integral of (90), will be obtained, in contrast to the general solution resulting from the inclusion of the arbitrary constants.

By analogy to (92), the general formula for solution of (87) is seen to be

$$y = e^{r_n x}\int e^{(r_{n-1} - r_n)x}\int \cdots \int e^{(r_2 - r_1)x}\int e^{-r_1 x}Q\,(dx)^n \tag{93}$$

Application of formula (93) is known as the "method of iteration." As might be expected, the successive integrations required by this formula may become so tedious and involved, particularly when a constant is inserted after every integration, that another method known as the "method of partial fractions" is often simpler.

If the operator in (87) is decomposed into partial fractions* such that

$$\frac{1}{(D - r_1)(D - r_2)\cdots(D - r_n)}Q = \left[\frac{A_1}{D - r_1} + \frac{A_2}{D - r_2} + \cdots + \frac{A_n}{D - r_n}\right]Q \tag{94}$$

* Decomposition into partial fractions is accomplished by assuming the solution in the form shown, clearing of fractions, and equating coefficients of like powers of D, whereupon enough equations will be available to determine the constants A.

a solution may be written

$$y = A_1\left(\frac{1}{D - r_1}\right)Q + A_2\left(\frac{1}{D - r_2}\right)Q + \cdots A_n\left(\frac{1}{D - r_n}\right)Q$$

and by (88) the terms on the right may be written

$$y = A_1 e^{r_1 x}\int e^{-r_1 x}Q\,dx + A_2 e^{r_2 x}\int e^{-r_2 x}Q\,dx + \cdots A_n\int e^{-r_n x}Q\,dx \tag{95}$$

Attention must be called to the fact that the constants A, resulting from decomposition of the operator into partial fractions, are absolute and not arbitrary, so that (95) is a particular integral of (83).

In many cases, instead of attempting to obtain the general solution directly by the method of iteration, it is more convenient to make use of Property I, Par. 50, and seek the complementary function and a particular integral.

52. Determination of the Complementary Function. The reduced equation associated with (83) may be written

$$(D - r_1)(D - r_2)\cdots(D - r_n)y = 0 \tag{96}$$

Obviously this equation may be satisfied if any one of the factors operating on y becomes zero. Hence,

$$(D - r_1)y = 0 \tag{97}$$

from which $y = C_1 e^{r_1 x}$, C_1 being an arbitrary constant. Similarly, $(D - r_n)y = 0$, and another solution is $y = C_n e^{r_n x}$. As indicated by Property II, Par. 50, the sum of all these solutions

$$y = C_1 e^{r_1 x} + C_2 e^{r_2 x} + \cdots C_n e^{r_n x} \tag{98}$$

is a solution and it is the general solution of (96), because it contains n independent arbitrary constants. Since it is the general solution of the reduced equation, it is the complementary function of (83).

A special case arises when two or more of the roots r are equal. In this case, the method of iteration indicates the nature of that part of the solution due to the equal roots. If $r_1 = r_2$, that part of the solution due to these roots may be written

$$(D - r_1)(D - r_1)y = 0$$

Application of (93), if the constant is inserted after each integration, gives

$$(D - r_1)y = C_1e^{r_1x}\int e^{-r_1x}(0)dx + C_1e^{r_1x} = C_1e^{r_1x}$$

$$y = \frac{1}{(D - r_1)}C_1e^{r_1x} = e^{r_1x}\int e^{-r_1x}C_1e^{r_1x}dx + C_2e^{r_1x}$$

$$= C_1xe^{r_1x} + C_2e^{r_1x}$$

$$= (C_1x + C_2)e^{r_1x} \tag{99}$$

If t roots are equal to r_1, repeated application of the iteration formula shows that the part of the solution due to these roots is

$$(C_1 + C_2x + \cdots C_tx^{t-1})e^{r_1x}$$

Another special case arises when some of the roots of (96) are imaginary. It is established in algebra that if imaginary roots occur, they occur in conjugate pairs, so that if there is one root $\alpha + i\beta$, there will be another $\alpha - i\beta$. If these two roots of the operator are designated as r_1 and r_2, the part of the solution due to them may be written

$$C_1e^{r_1x} + C_2e^{r_2x} = C_1e^{(\alpha+i\beta)x} + C_2e^{(\alpha-i\beta)x} \tag{100}$$

By suitable transformation, this part of the solution may be placed in a much more convenient form, and at the same time its imaginary appearance may be removed.

In Chap. V, it is shown how e^u may be expanded in a Maclaurin's series to give

$$e^u = 1 + u + \frac{u^2}{2!} + \frac{u^3}{3!} + \frac{u^4}{4!} + \cdots \tag{101}$$

$e^{\alpha+i\beta}$ may be written $e^\alpha \cdot e^{i\beta}$, and when $u = i\beta$

$$e^{i\beta} = 1 + i\beta + \frac{i^2\beta^2}{2!} + \frac{i^3\beta^3}{3!} + \frac{i^4\beta^4}{4!} + \cdots \tag{102}$$

On the basis that $i^2 = -1$, $i^3 = -i$, $i^4 = 1$, etc., this may be written

$$e^{i\beta} = 1 + i\beta - \frac{\beta^2}{2!} - \frac{i\beta^3}{3!} + \frac{\beta^4}{4!} + \frac{i\beta^5}{5!} - \frac{\beta^6}{6!} + \cdots \tag{103}$$

Collecting real and imaginary parts gives

$$e^{i\beta} = 1 - \frac{\beta^2}{2!} + \frac{\beta^4}{4!} - \frac{\beta^6}{6!} + \cdots i\left(\beta - \frac{\beta^3}{3!} + \frac{\beta^5}{5!} - \frac{\beta^7}{7!} + \frac{\beta^9}{9!} \cdots\right) \tag{104}$$

But $\sin \beta$ expanded in Maclaurin's series is

$$\sin \beta = \beta - \frac{\beta^3}{3!} + \frac{\beta^5}{5!} - \frac{\beta^7}{7!} + \frac{\beta^9}{9!} + \cdots \tag{105}$$

and

$$\cos \beta = 1 - \frac{\beta^2}{2!} + \frac{\beta^4}{4!} - \frac{\beta^6}{6!} + \cdots \tag{106}$$

Therefore,

$$e^{i\beta} = \cos \beta + i \sin \beta \tag{107}$$

$$e^{\alpha x} e^{i\beta x} = e^{\alpha x}(\cos \beta x + i \sin \beta x) \tag{108}$$

Similarly, it should be clear that $e^{-i\beta} = (\cos \beta - i \sin \beta)$, so that $e^{(\alpha - i\beta)x} = e^{\alpha x} e^{-i\beta x} = e^{\alpha x}(\cos \beta x - i \sin \beta x)$. If these substitutions are made, the part of the solution due to the imaginary roots may be written

$$C_1 e^{(\alpha + i\beta)x} + C_2 e^{(\alpha - i\beta)x} = e^{\alpha x}[(C_1 + C_2) \cos \beta x + i(C_1 - C_2) \sin \beta x] \tag{109}$$

When $C_1 + C_2 = A$, and $i(C_1 - C_2) = B$, the right side of (109) becomes

$$e^{\alpha x}(A \cos \beta x + B \sin \beta x) \tag{110}$$

Inasmuch as C_1 and C_2 are arbitrary, by assigning proper imaginary values to them it is possible to make A and B assume any desired real values. A and B are therefore arbitrary constants, which may be assigned any real values.

As an example of a simple equation giving rise to imaginary roots, let us solve

$$\frac{d^2y}{dx^2} + y = 3 \tag{111}$$

Even though (111) is an equation not containing x and may be solved by the method of Par. 49, it will be instructive and considerably less trouble to solve it by the methods that have just been discussed. When this is written in the operational form,

$$(D^2 + 1)y = 3 \tag{112}$$

The complementary function is the general solution of the reduced equation

$$(D^2 + 1)y = 0 \tag{113}$$

Since the roots of $(D^2 + 1) = 0$ are $D = \pm i$, (113) may be written

$$(D + i)(D - i)y = 0 \tag{114}$$

so that if $r_1 = \alpha + i\beta$ and $r_2 = \alpha - i\beta$, $\alpha = 0$ and $\beta = 1$. According to (110), the general solution of (114) then becomes

$$y = A \cos x + B \sin x \tag{115}$$

Equation (115) is the complementary function of (111), and to complete the general solution it is necessary to determine a particular integral. By inspection, it may be seen that $y = 3$ will satisfy (111), so that by Property I, Par. 50, the general solution of (111) is

$$y = A \cos x + B \sin x + 3 \tag{116}$$

The particular integral was obtained with unusual ease in this example, and completion of the discussion of linear equations awaits description of additional methods for obtaining particular integrals.

53. Determination of the Particular Integral. Two methods have already been given in Par. 51 for determination of a particular integral of the general equation (83), *viz.*, the method of iteration with constants placed equal to zero after each integration, and the method of partial fractions. Other methods of less general applicability but of considerably greater utility in many cases will now be described.

When the particular integral cannot be determined by inspection, recourse may be had to the method of undetermined coefficients, best illustrated by solution of the example that follows:

$$\frac{d^2y}{dx^2} - K^2y = f(x) = x^3 + x^2 \tag{117}$$

The complementary function is obtained by solving the reduced equation

$$\frac{d^2y}{dx^2} - K^2y = 0 \tag{118}$$

which is the same as Eq. (55) developed in Chap. II for the description of simultaneous absorption and first-order chemical reaction, K^2 being placed equal to $k\ D$. If (118) is written in the operational form

$$(D - K)(D + K)y = 0 \tag{119}$$

its general solution may be written as

$$y = C_1 e^{-Kx} + C_2 e^{Kx} \tag{120}$$

Completion of the general solution requires determination of a particular integral of (117). Make a table of $f(x)$ and its derivatives.

$$\begin{aligned} f(x) &= x^3 + x^2 \\ f'(x) &= 3x^2 + 2x \\ f''(x) &= 6x + 2 \\ f'''(x) &= 6 \end{aligned}$$

The linearly independent functions in this table are x^3, x^2, and x, for it is impossible to find any set of constants such that $C_1x^3 + C_2x^2 + C_3x$ equals zero for all values of x. It will be assumed that the particular integral may be expressed as a linear function of these linearly independent functions, *i.e.*,

$$I = ax^3 + bx^2 + cx + d \tag{121}$$

The values of the coefficients may now be determined by substitution in the original equation and comparison of like powers of x.

$$\frac{dI}{dx} = 3ax^2 + 2bx + c$$

$$\frac{d^2I}{dx^2} = 6ax + 2b$$

$$6ax + 2b - K^2(ax^3 + bx^2 + cx + d) = x^3 + x^2 \tag{122}$$

$$-K^2a = 1 \text{ (condition on coefficients of } x^3)$$

$$-K^2b = 1 \text{ (condition on coefficients of } x^2)$$

$$6a - K^2c = 0 \text{ (condition on coefficients of } x)$$

$$2b - K^2d = 0 \text{ (condition on coefficients of } x^0)$$

These equations give: $a = -\frac{1}{K^2}$; $b = -\frac{1}{K^2}$; $c = \frac{6a}{K^2} = -\frac{6}{K^4}$; $d = \frac{2b}{K^2} = -\frac{2}{K^4}$; and the particular integral is

$$I = -\frac{x^3}{K^2} - \frac{x^2}{K^2} - \frac{6x}{K^4} - \frac{2}{K^4} \tag{123}$$

The following equation then is the general solution of (117):

$$y = C_1 e^{-Kx} + C_2 e^{Kx} - \frac{x^3}{K^2} - \frac{x^2}{K^2} - \frac{6x}{K^4} - \frac{2}{K^4} \tag{124}$$

The method just illustrated will work so long as the derivatives of $f(x)$ are finite in number and linearly independent. A slight

modification of the foregoing procedure is necessary in case any of the functions in $f(x)$ and its derivatives appear in the complementary function. Suppose that we must solve

$$\frac{d^2y}{dx^2} - K^2y = e^{Kx} + \sin x \tag{125}$$

The complementary function is the same as in the previous example. The table of $f(x)$ and its derivatives shows

$$\begin{aligned} f(x) &= e^{Kx} + \sin x \\ f'(x) &= Ke^{Kx} + \cos x \\ f''(x) &= K^2e^{Kx} - \sin x \\ f'''(x) &= K^3e^{Kx} - \cos x \end{aligned}$$

The only linearly independent functions here are $\sin x$, $\cos x$, and e^{Kx}, the last having already appeared in the complementary function. If we assume that

$$I = ae^{Kx} + b \sin x + c \cos x + d$$

the term ae^{Kx} will be lost on substitution into the left-hand side of (125) since it is a particular solution of the reduced equation. The method may still be applied if the term or terms that are part of the complementary function are multiplied by the lowest power of x necessary to make them different from any term in the complementary function.

If this procedure is followed, the particular integral in the present case will be assumed to be

$$\begin{aligned} I &= axe^{Kx} + b \sin x + c \cos x + d \\ \frac{dI}{dx} &= aKxe^{Kx} + ae^{Kx} + b \cos x - c \sin x \\ \frac{d^2I}{dx^2} &= aK^2xe^{Kx} + 2aKe^{Kx} - b \sin x - c \cos x \end{aligned}$$

Substituting in (125) results in

$$2aKe^{Kx} - b(1 + K^2) \sin x - c(1 + K^2) \cos x - K^2d = e^{Kx} + \sin x \tag{126}$$

$$2aK = 1; \qquad a = \frac{1}{2K}$$

$$-b(1 + K^2) = 1; \qquad b = -\frac{1}{1 + K^2}$$

$$-c(1 + K^2) = 0; \qquad c = 0; \qquad -K^2d = 0, \qquad d = 0$$

$$I = \frac{x}{2K}e^{Kx} - \frac{1}{1 + K^2}(\sin x) \tag{127}$$

and the general solution of (126) is

$$y = C_1 e^{-Kx} + C_2 e^{Kx} + \frac{x}{2K} e^{Kx} - \frac{1}{1 + K^2} \sin x \qquad (128)$$

Other methods of determining the particular integral are available in more advanced treatises. For instance, Lagrange's method of variation of parameters* is a general procedure for determining a particular integral when the complementary function is known. It is of particular value in equations with variable coefficients. Fortunately, the method of undetermined coefficients and the two operational methods of iteration and partial fractions are sufficient for many equations arising in practice.

54. The Euler Equation. A Type Reducible to a Linear Equation with Constant Coefficients. The solution of the linear equation

$$x^n \frac{d^n y}{dx^n} + a_1 x^{n-1} \frac{d^{n-1} y}{dx^{n-1}} + \cdots a_{n-1} x \frac{dy}{dx} + a_n y = f(x)$$

can be reduced to the solution of an equation with constant coefficients by the substitution $x = e^z$. The method may be illustrated by solution of the equation

$$x^3 \frac{d^3 y}{dx^3} + x \frac{dy}{dx} = \ln x \qquad (129)$$

$$\frac{dy}{dx} = \frac{dy}{dz} \cdot \frac{dz}{dx} = \frac{dy}{dz} e^{-z}$$

$$\frac{d^2 y}{dx^2} = \frac{dz}{dx} \cdot \frac{d}{dz}\left(e^{-z} \cdot \frac{dy}{dz}\right) = e^{-2z} \cdot \frac{d^2 y}{dz^2} - e^{-2z} \cdot \frac{dy}{dz}$$

$$\frac{d^3 y}{dz^3} = \frac{dz}{dx} \cdot \frac{d}{dz}\left(e^{-2z} \frac{d^2 y}{dz^2} - e^{-2z} \frac{dy}{dz}\right)$$

$$= e^{-3z} \frac{d^3 y}{dz^3} - 2e^{-3z} \frac{d^2 y}{dz^2} - e^{-3z} \frac{d^2 y}{dz^2} + 2e^{-3z} \frac{dy}{dz}$$

$$= e^{-3z} \frac{d^3 y}{dz^3} - 3e^{-3z} \frac{d^2 y}{dz^2} + 2e^{-3z} \frac{dy}{dz}$$

Substituting these values in (129) gives

$$\frac{d^3 y}{dz^3} - 3\frac{d^2 y}{dz^2} + 3\frac{dy}{dz} = z \qquad (130)$$

* "Higher Mathematics for Engineers and Physicists," SOKOLNIKOFF, I. S., and E. S. SOKOLNIKOFF, p. 282, McGraw-Hill Book Company, Inc., New York, 1934.

The reduced equation is

$$(D^3 - 3D^2 + 3D)y = D(D^2 - 3D + 3)y = 0 \qquad (131)$$

The second factor has two imaginary roots obtainable from the quadratic formula

$$D = \frac{3 \pm \sqrt{9 - 12}}{2} = \frac{3 \pm \sqrt{3}i}{2}$$

(131) may then be written in the standard form

$$(D - 0)\left[D - \left(1.5 - \frac{\sqrt{3}}{2}i\right)\right]\left[D - \left(1.5 + \frac{\sqrt{3}}{2}i\right)\right]y = 0$$

If the imaginary roots are written $\alpha \pm i\beta$, $\alpha = 1.5$ and $\beta = \sqrt{3}/2$.

When the trigonometric form (Par. 52) for that part of the solution due to the imaginary roots is used, the complementary function is

$$y = C_1 + e^{(1.5)z}\left(A \sin \frac{\sqrt{3}}{2}z + B \cos \frac{\sqrt{3}}{2}z\right) \qquad (132)$$

A particular integral will be determined by the method of undetermined coefficients. In this case,

$$f(z) = z, \qquad f'(z) = 1, \qquad f''(z) = 0$$

When the particular integral is taken as

$$I = az + b$$

it is seen that a constant occurs alone, and since a constant has already occurred alone in the complementary function, it is necessary to multiply by z (Par. 53), obtaining $I = az^2 + bz$. $dI/dz = 2az + b$; $d^2I/dz^2 = 2a$; $d^3I/dz^3 = 0$. Substituting in (130) gives

$$-6a + 6az + 3b = z$$

Therefore

$$-6a + 3b = 0, \qquad \text{and} \qquad 6a = 1; \qquad a = \tfrac{1}{6}; \qquad b = \tfrac{1}{3}.$$

$$I = \tfrac{1}{6}z^2 + \tfrac{1}{3}z$$

We may now write the general solution of (130) as

$$y = C_1 + e^{(1.5)z}\left(A \sin \frac{\sqrt{3}}{2}z + B \cos \frac{\sqrt{3}}{2}z\right) + \frac{1}{6}z^2 + \frac{1}{3}z$$

Reversion to the original variable x gives the general solution of (129)

$$y = C_1 + x^{1.5}\left[A \sin\left(\frac{\sqrt{3}}{2} \ln x\right) + B \cos\left(\frac{\sqrt{3}}{2} \ln x\right)\right] + \frac{(\ln x)^2}{6} + \frac{\ln x}{3} \quad (133)$$

55. The Second-order Equation. The second-order equation occurs so frequently that this section will be devoted to a summary of the methods available for its solution.

1. If the equation is one in which any of the terms x, y, and dy/dx are absent, it may be attacked by the methods of Par. 49 and reduced to a first-order equation.

2. If the equation is linear, its general solution will consist of the sum of the complementary function and a particular integral. If the equation is one with constant coefficients, the complementary function is obtained by the method of Par. 52 and the particular integral by the method of Par. 53.

Since all of the arbitrary constants are contained in the complementary function, no constant of integration should be appended to the particular integral.

3. If any solution of the reduced equation is known, it is possible to convert the original equation into a linear equation of the first order which may always be solved by the method of Par. 42. This conversion proceeds by the substitution illustrated under Property III, Par. 50. Unfortunately, no general method exists for determining a solution of the reduced equation with variable coefficients.

4. If the equation as originally presented falls into none of the preceding cases, it may sometimes be made to fall under one of them by means of special substitutions and a change in variable.

5. Very frequently equations will occur that are insoluble by any of the previous methods. In these cases, it is necessary to resort to solution by series or to one of the graphical or numerical methods to be outlined later. Certain equations that must be solved in series occur so frequently in applied mathematics that they have been subjected to special study with the result that the series to which they give rise are now well-known functions. The Bessel functions to be discussed in Chap. V

are an example of functions necessary to the solution of a type of equation occurring very frequently.

56. Determination of Particular Solutions from the Boundary Conditions. From the standpoint of mathematical theory, a differential equation is considered solved when the dependent variable is expressed as a function of the independent variable in terms of either known functions or integrals, even though the integrals may not be expressible in terms of functions already known. From the standpoint of practical application, however, this mathematical solution is of value only in a qualitative way until it is in such a form that it may be made to yield actual numerical values of the two variables over the ranges of interest. Placing the equation in this form usually requires the determination of such values of the arbitrary constants that the equation will fit the given boundary conditions. This procedure has already been illustrated in Chap. II with several simple first-order equations, and we shall now illustrate it with a second-order equation.

In Par. 29, in connection with heat transfer along a thin fin connecting a heat source and sink, the differential equation relating the difference x along the fin to the temperature t was shown to be

$$\frac{d^2t}{dx^2} = \frac{UP}{kA}(t - t_s) \tag{134}$$

t_s being the temperature of the surroundings. U, the heat-transfer coefficient to the surroundings, is to be taken constant at 2.0 B.t.u./(hr.)(sq. ft.)(°F.), and k is constant at 220 (B.t.u.)(ft.)/(hr.)(sq. ft.)(°F.). Let the width of the fin be W ft. As the fin is 0.1 in. thick, the cross-sectional area will be $(0.1/12)W$ sq. ft.; and if W is taken large compared to 0.1 in., the perimeter of the fin P will be $2W$, and $P/A = 24/0.1 = 240$. For purposes of solution, place $UP/kA = a^2$. Note that when t_s is constant, $d(t - t_s)/dx = dt/dx$, and $d^2(t - t_s)/dx^2 = d^2t/dx^2$. Equation (134) may therefore be written

$$\frac{d^2(t - t_s)}{dx^2} - a^2(t - t_s) = 0$$

The solution may be written down immediately by the methods of Par. 51 and is

$$(t - t_s) = C_1e^{ax} + C_2e^{-ax} \tag{135}$$

This equation will now be used to plot a curve of fin temperature vs. distance from the hot source. If t_1 is the temperature of the hot source, it is clear that when $t - t_s = t_1 - t_s$, $x = 0$, and (136) reduces to

$$t_1 - t_s = C_1 + C_2 \tag{136}$$

If t_2 is the temperature of the heat sink and L the length of the fin, then for $t - t_s = t_2 - t_s$ we have

$$t_2 - t_s = C_1 e^{aL} + C_2 e^{-aL} \tag{137}$$

This may be written in a simpler form if the hyperbolic functions are employed.*

When C_1 is eliminated by (136),

$$t_2 - t_s = (t_1 - t_s - C_2)e^{aL} + C_2 e^{-aL} \tag{138}$$

$$C_2 = \frac{(t_1 - t_s)e^{aL} - (t_2 - t_s)}{e^{aL} - e^{-aL}} = \frac{(t_1 - t_s)e^{aL} - (t_2 - t_s)}{2 \sinh aL} \tag{139}$$

$$C_1 = (t_1 - t_s) - C_2 =$$

$$\frac{(t_1 - t_s)(e^{aL} - e^{-aL}) - (t_1 - t_s)e^{aL} + (t_2 - t_s)}{2 \sinh aL}$$

$$= \frac{(t_2 - t_s) - (t_1 - t_s)e^{-aL}}{2 \sinh aL} \tag{140}$$

Substituting these values for C_1 and C_2 into (135) gives

$$t - t_s = \frac{[(t_2 - t_s) - (t_1 - t_s)e^{-aL}]e^{ax} + [(t_1 - t_s)e^{aL} - (t_2 - t_s)]e^{-ax}}{2 \sinh aL} \tag{141}$$

* By definition, the hyperbolic sine of x (written sinh x) is

$$\sinh x = \frac{e^x - e^{-x}}{2}$$

and the hyperbolic cosine of x (written cosh x) is defined as

$$\cosh x = \frac{e^x + e^{-x}}{2}$$

It may be shown from the series defining the hyperbolic functions that they are analogous to the corresponding trigonometric functions. Tables of the hyperbolic functions are available in all standard handbooks

This may be written

$$t - t_s = \frac{(t_2 - t_s)(e^{ax} - e^{-ax}) + (t_1 - t_s)(e^{a(L-x)} - e^{-a(L-x)})}{2 \sinh aL} \quad (142)$$

$$t - t_s = \frac{(t_2 - t_s) \sinh ax + (t_1 - t_s) \sinh a(L - x)}{\sinh aL} \quad (143)$$

Equation (143) is in convenient form for calculation of a curve of t vs. x, as tables of hyperbolic sines are readily available.

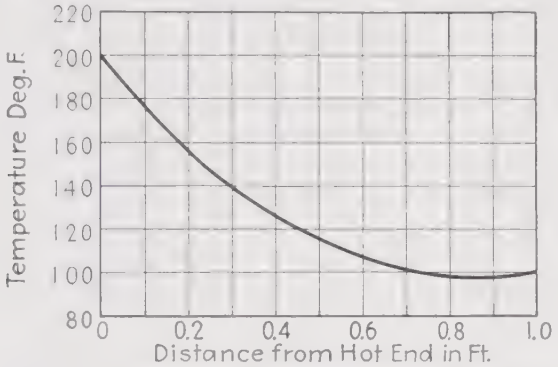

FIG. 34.—Temperature distribution along metal fin.

L, the length of the fin, will be taken as 1 ft., and

$$a = \sqrt{\frac{UP}{kA}} = \sqrt{\frac{2(240)}{220}} = 1.48$$

Since $t_s = 0°\text{F.}$, $(t_2 - t_s) = 100$ and $(t_1 - t_s) = 200$. We then have

$$t - 0 = t = \frac{100 \sinh 1.48x}{\sinh 1.48} + \frac{200 \sinh 1.48(1 - x)}{\sinh 1.48} \quad (144)$$

From tables, $\sinh 1.48 = 2.083$. Therefore, the particular solution of (134) applying to the given boundary conditions is

$$t = 47.9 \sinh 1.48x + 95.8 \sinh 1.48(1 - x) \quad (145)$$

Corresponding values of t and x appear in the following table and are plotted on Fig. 34.

TABLE V

x (ft.)	T(°F.)
0	200.0
0.2	156.3
0.4	126.7
0.6	108.4
0.8	99.4
0.9	99.2
1.0	100.0

It is interesting to note that this curve goes through a minimum near the cold end of the fin. The greater the value of a^2 in (134), the more pronounced will be this minimum. When $a^2 = 0$, (135) reduces to $d^2t/dx^2 = 0$, the differential equation of a straight line. Thus Eq. (134) is in conformity with the heat-transfer theory which would predict a straight line gradient along the fin if the latter were perfectly insulated, corresponding to a value of zero for the surface heat-transfer coefficient.

57. Example of Consecutive Reversible Reactions. As a final example of the determination of constants, we shall solve Eq. (81) of Chap. II. When $(k_1 + k_2 + k_3 + k_4) = a$ and $(k_1k_3 + k_2k_4 + k_1k_4) = b$ this equation may be written

$$(D^2 + aD + b)x = k_2k_4 \tag{146}$$

The roots of $D^2 + aD + b = 0$ are obtained by the quadratic formula and are

$$r_1 = \frac{-a - \sqrt{a^2 - 4b}}{2}$$

$$r_2 = \frac{-a - \sqrt{a^2 - 4b}}{2}$$

Therefore, the reduced equation may be written

$$(D - r_1)(D - r_2)x = 0 \tag{147}$$

and the complementary function is

$$x = C_1e^{-r_1\theta} + C_2e^{-r_2\theta} \tag{148}$$

The particular integral obtainable by inspection or by the method of undetermined coefficients is k_2k_4/b, and the general solution is

$$x = C_1e^{-r_1\theta} + C_2e^{-r_2\theta} + \frac{k_2k_4}{b} \tag{149}$$

The two arbitrary constants may be determined from the conditions that when $\theta = 0$, $x = 1$, $y = 0$, $z = 0$, and $dz/d\theta = 0$. Placing $\theta = 0$ and $x = 1$ in (149) gives

$$1 = C_1 + C_2 + \frac{k_2k_4}{b} \tag{150}$$

Differentiation of (148) on the basis that $x = 1 - z - y$ results in

$$\frac{dx}{d\theta} = -\frac{dz}{d\theta} - \frac{dy}{d\theta} = -r_1C_1e^{-r_1\theta} - r_2C_2e^{-r_2\theta} \tag{151}$$

But from Eq. (78) of Chap. II

$$\frac{dy}{d\theta} = -(k_2 + k_3)y + k_1x + k_4z$$

and, when $\theta = 0$, $dy/d\theta = k_1$.
Substituting $\theta = 0$ in (151) produces

$$\begin{aligned} r_1C_1 + r_2C_2 &= k_1 \\ C_1 &= \frac{k_1 - r_2C_2}{r_1} \end{aligned} \tag{152}$$

Substituting for C_1 in (150) and solving for C_2 give

$$C_2 = \frac{1 - \dfrac{k_1}{r_1} - \dfrac{k_2k_4}{b}}{1 - \dfrac{r_2}{r_1}} \tag{153}$$

Both arbitrary constants have now been determined in terms of the reaction-rate constants.

58. Systems of Simultaneous Differential Equations. The solution of a set of differential equations involving one independent variable and a number of dependent variables equal to the number of equations n may be made to depend upon the solution of a differential equation of order n. Sets of two simultaneous differential equations have already been encountered in Pars. 32 and 35. The method of elimination employed in Par. 32 is of general applicability, but, when the equations are linear with constant coefficients, the differential operators introduced in Par. 51 of the present chapter provide a more convenient method of treatment. The method will be applied to the solution of Eqs. (77) and (78) of Chap. II. The set of equations to be solved is

$$\begin{aligned} \frac{dx}{d\theta} &= -k_1x + k_2y \\ \frac{dy}{d\theta} &= -(k_2 + k_3)y + k_1x + k_4(1 - x - y) \end{aligned}$$

These may be written

$$(D + k_1)x = k_2 y \tag{154}$$

$$(D + k_2 + k_3 + k_4)y = (k_1 - k_4)x + k_4 \tag{155}$$

It is now possible to proceed with the elimination of either x or y in a manner similar to that used in solving simultaneous algebraic equations.

When (154) is solved for y,

$$y = \frac{(D + k_1)x}{k_2}$$

Substituting in (155) results in

$$(D + k_2 + k_3 + k_4)(D + k_1)x = (k_2)(k_1 - k_4)x + k_4 k_2 \tag{156}$$

Upon performance of the indicated operations of differentiation

$$(D + k_2 + k_3 + k_4)(D + k_1)x = D^2x + (k_1 + k_2 + k_3 + k_4)Dx + (k_1k_2 + k_1k_3 + k_1k_4)x = \frac{d^2x}{d\theta^2} + (k_1 + k_2 + k_3 + k_4)\frac{dx}{d\theta} + (k_1k_2 + k_1k_3 + k_1k_4)x$$

Substitution into (156) and collection of terms give (81), Chap. II.

GRAPHICAL AND NUMERICAL METHODS FOR SOLUTION OF DIFFERENTIAL EQUATIONS

59. The General Problem. Because of the complexity of the functions encountered in many chemical engineering processes, particularly those functions representing thermodynamic and kinetic data, the differential equations encountered are often incapable of solution by the methods presented in the preceding sections. In such cases, it is necessary to resort to one of the many so-called "approximate methods" of solution. Although these do not lead to analytical solutions, it is possible to calculate numerical values for particular solutions to any desired number of significant figures.

Solution is always possible by means of series expansion, to be discussed in Chap. V, but these frequently become unwieldy and require considerable experience in use. On the other hand, the graphical and numerical methods now to be discussed are fundamentally very simple and are applicable to ordinary differential equations of any order. They are of particular value in complex design problems.

If an equation of the first order is expressed in the form

$$\frac{dy}{dx} = f(x,y) \tag{157}$$

its solution may be expressed as

$$y = \int f(x,y)dx + c \tag{158}$$

Let it be specified that a particular solution must pass through the point $x = x_0$, $y = y_0$, and (158) becomes

$$y = y_0 + \int_{x_0}^{x} f(x,y)dx \tag{159}$$

an equivalent form of which is

$$y = y_0 + \int_{x_0}^{x} \left(\frac{dy}{dx}\right)dx \tag{160}$$

Equations (159) and (160) are known as "integral equations," because both variables appear under the integral sign and their direct exact solution by means of ordinary quadrature formulas, which contain only one variable, is impossible. It will be shown, however, that by several alternative methods of successive approximation the solution may be obtained to any desired degree of accuracy provided that several simple conditions are fulfilled.

60. Modified Euler Method. Starting at the point x_0, y_0, determine the increment in y for a given increment in x. If the increment to be calculated is small, the corresponding portion of the y, x curve to be calculated will approximate a straight line. This means that the value of dy/dx over this interval remains nearly constant at its value calculated at the beginning of the interval. Granting these conditions, (159) and (160) may be integrated to give

$$y_1^{(1)} = y_0 + \left(\frac{dy}{dx}\right)_0 (x_1 - x_0) = y_0 + f(x_0,y_0)(x_1 - x_0) \tag{161}$$

$y_1^{(1)}$ will denote the first approximation to the true value of y at x_1. When $y_1^{(1)}$ is calculated, a new interval may be taken and (161) applied to give

$$y_2^{(1)} = y_1^{(1)} + \left(\frac{dy}{dx}\right)_1 (x_2 - x_1) = y_1 + f(x_1,y_1^{(1)})(x_2 - x_1) \tag{162}$$

This process, repeated a sufficient number of times, will yield y as a function of x over the desired interval. A great disadvantage of the method lies in the fact that, if dy/dx is changing rapidly over an interval, its value at the beginning of the interval may be a poor approximation for its average value over the interval, and $y_1^{(1)}$ may be much in error compared with the true value. Errors of this nature accumulate with succeeding intervals until the value of y becomes so much in error as to be completely useless. Figure 35 shows a plot of the exponential

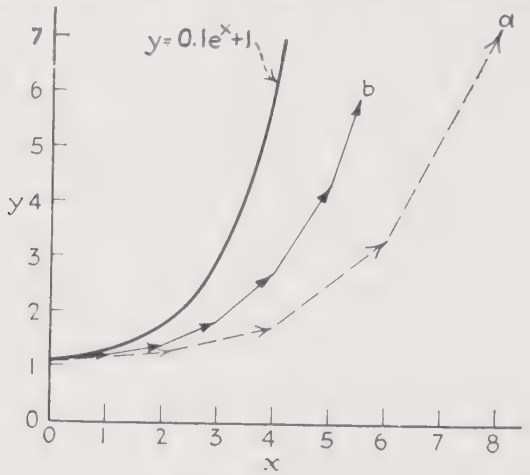

FIG. 35.—Solution of a differential equation by method of finite increments.

function $y = 0.1e^x + 1$, which is a particular solution of the equation

$$\frac{dy}{dx} = y - 1 \tag{163}$$

passing through the point (0, 1.1). The dotted line connecting a series of arrows shows the result of Euler's method when the increment in x is taken as 2 and the value of dy/dx taken as its value at the beginning of each interval. If the increment is halved, the approximation as indicated by curve b is better but still inadmissible.

An improved result may be effected by either or a combination of two methods:

1. Decreasing the size of the increment Δx.
2. Using a better value for the average value of $dy/dx = f(x,y)$ over each interval.

Each of the following methods to be discussed has as its basis for an improvement in accuracy the use of a better average

value for the slope dy/dx over each interval. Regardless of the method used, it is usually possible to secure an improvement in the accuracy of this stepwise process by decreasing the size of the interval $(x_n - x_{n-1})$, although this improvement in accuracy is secured at the expense of considerable additional labor in calculation.

The most obvious method of obtaining a better average value for dy/dx is to repeat the calculation represented by Eq. (161) several times, using for dy/dx in each successive calculation its arithmetic average value obtained at the beginning and end of the interval. Such a calculation would proceed as follows for the interval $(x_1 - x_0)$:

$$y_1^{(1)} = y_0 + \left(\frac{dy}{dx}\right)_0 (x_1 - x_0) = y_0 + f(x_0,y_0)(x_1 - x_0) \quad (164)$$

$$y_1^{(2)} = y_0 + \left(\frac{dy}{dx}\right)_{\text{av}}^{(1)} (x_1 - x_0); \qquad \left(\frac{dy}{dx}\right)_{\text{av}}^{(1)} = \frac{f(x_0,y_0) + f(x_1,y_1^{(1)})}{2}$$

and the kth approximation becomes

$$y_1^{(k)} = y_0 + \left(\frac{dy}{dx}\right)_{\text{av}}^{(k-1)} (x_1 - x_0); \quad \left(\frac{dy}{dx}\right)_{\text{av}}^{(1)} = \frac{f(x_0,y_0) + f(x_1,y_1^{(k-1)})}{2}$$

In practice, if the size of the interval is reasonably small, there is ordinarily but little difference between the successive values of y after the first few approximations.

As an illustration of how this process may be carried out systematically, an integral curve of Eq. (163) through the point (0, 1.1) appears in Table VI, where subscripts a and b refer to the beginning and the end of an interval, respectively.

NOTATION FOR NUMERICAL SOLUTIONS

Point 0	Point 1	Point 2	Point 3	Point 4	Point 5
x_0	x_1	x_2	x_3	x_4	x_5
Interval 1	Interval 2	Interval 3	Interval 4	Interval 5	
x_a	x_b	x_a	x_b	x_a	x_b
					etc.
	x_a	x_b	x_a	x_b	

The accompanying tabulation is helpful in understanding the notation referring to points and intervals in the tables explaining solution by the various numerical methods. Point 0 is the point at which calculation starts and point 1 is at the end of interval 1. The column number in the tables is the interval number. Thus,

x_b in column 3 refers to point 3; both x_b in column 4 and x_a in column 5 refer to point 4.

The arrowheads in Fig. 36 indicate the results of several successive approximations, the top arrow being $y_b^{(5)}$ for every interval but the fourth. For an interval of 1, this represents a better approximation than was obtained in curve *b* of Fig. 35. There is a bad divergence on the other side of the theoretical curve in this case, although the agreement could be considerably improved if the interval Δx were to be made smaller. Instead of making the interval smaller, however, we shall proceed to an improved method of evaluating dy/dx over each interval.

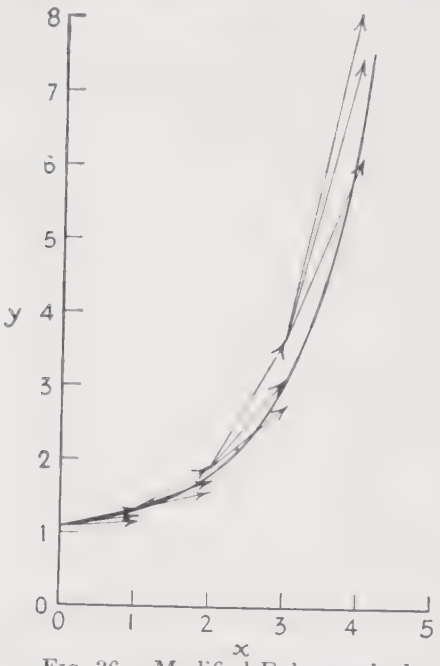

FIG. 36.—Modified Euler method.

61. The Picard Process. If in Eq. (159) we consider y constant over the interval $x_0 - x_1$, at its initial value y_0, the integrand becomes $f(x,y_0)$ and is a function of x alone; the first approximation for y_1 is

$$y_1^{(1)} = y_0 + \int_{x_0}^{x_1} f(x,y_0)dx \quad (165)$$

If $y_1^{(1)}$ is inserted in the integrand in place of y_0, we obtain a second approximation to the true value of y_1, and $y_1^{(2)}$ is obtained.

$$y_1^{(2)} = y_0 + \int_{x_0}^{x_1} f(x,y_1^{(1)})dx \quad (166)$$

In the same manner, it is possible to proceed to the kth approximation

$$y_1^{(k)} = y_0 + \int_{x_0}^{x_1} f(x,y_1^{(k-1)})dx \quad (167)$$

Although readily shown, it will be stated here without proof that the successive approximations for y_1 will converge to the theoretically correct value if

$$x_1 - x_0 < \frac{1}{\left[\dfrac{\partial f(x,y)}{\partial y}\right]_{\max}} \quad (168)$$

where the denominator of the quantity on the right is the maximum value of $\partial f(x,y)/\partial y$ in the region $x_1 - x_0$, $y_1 - y_0$. A

TABLE VI

Interval	1	2	3	4
y_a	1.10	1.29	1.85	3.49
x_a	0.00	1.00	2.00	3.00
Δx	1.00	1.00	1.00	1.00
x_b	1.00	2.00	3.00	4.00
$\left(\frac{dy}{dx}\right)_a = y_a - 1$	0.10	0.29	0.85	2.49
$\left(\frac{dy}{dx}\right)_a \cdot \Delta x$	0.10	0.29	0.85	2.49
$y_b^{(1)}$	1.20	1.58	2.70	6.08
$\left(\frac{dy}{dx}\right)_{av}^{(1)} = \frac{y_a + y_b^{(1)} - 2}{2}$	0.15	0.43	1.26	3.83
$\left(\frac{dy}{dx}\right)_{av}^{(1)} \cdot \Delta x$	0.15	0.43	1.26	3.83
$y_b^{(2)}$	1.25	1.72	3.11	7.32
$\left(\frac{dy}{dx}\right)_{av}^{(2)} = \frac{y_a + y_b^{(2)} - 2}{2}$	0.17	0.51	1.48	4.40
$\left(\frac{dy}{dx}\right)_{av}^{(2)} \cdot \Delta x$	0.17	0.51	1.48	4.40
$y_b^{(3)}$	1.27	1.80	3.33	7.89
$\left(\frac{dy}{dx}\right)_{av}^{(3)} = \frac{y_a + y_b^{(3)} - 2}{2}$	0.18	0.55	1.59	4.69
$\left(\frac{dy}{dx}\right)_{av}^{(3)} \cdot \Delta x$	0.18	0.55	1.59	4.69
$y_b^{(4)}$	1.28	1.84	3.44	8.18
$\left(\frac{dy}{dx}\right)_{av}^{(4)} = \frac{y_a + y_b^{(4)} - 2}{2}$	0.19	0.56	1.64	
$\left(\frac{dy}{dx}\right)_{av}^{(4)} \Delta x$	0.19	0.56	1.64	
$y_b^{(5)}$	1.29	1.85	3.49	

similar statement holds for each succeeding interval. Let us apply this process to the solution of the equation

$$\frac{dy}{dx} = y - 1 \tag{163}$$

where $f(x,y) = y - 1$ and $y_0 = 1.1$, $x_0 = 0$.

Since $\partial(y-1)/\partial y = 1$, the value of each interval must be less than 1 if convergence to the true value of y is to be anticipated. The size of the interval being left indefinite for the time being, the successive approximations may be written

$$y_1^{(1)} = y_0 + \int_0^x (y_0 - 1)dx = 1.1 + \int_0^x (0.1)dx = 1.1 + 0.1x \quad (169)$$

$$y_1^{(2)} = 1.1 + \int_0^x (1.1 + 0.1x - 1)dx = 1.1 + 0.1x + \frac{0.1x^2}{2} \quad (170)$$

$$y_1^{(3)} = 1.1 + \int_0^x \left(1.1 + 0\,1x + \frac{0.1x^2}{2} - 1\right)dx = 1.1 + 0.1x + \frac{0.1x^2}{2} + \frac{0.1x^3}{2.3} \quad (171)$$

Continuing approximations will obviously develop the series

$$y_1 = 1 + 0.1\left(1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots \frac{x^n}{n!}\right) \quad (172)$$

But the series in parenthesis is exactly the series obtained when e^x is expanded in Maclaurin's series, so that (172) agrees with the exact solution $y = 1 + 0.1e^x$. When (172) is used to represent the solution, it must be remembered that the increment in x must not be greater than 1, *i.e.*,

$$x - x_0 = x - 0; \qquad x < 1$$

To calculate a value of y_2 in the interval $x = 1$, $x = 2$, we must first calculate some value of y in the interval $x = 0$, $x = 1$, and then write

$$y_2 = y_1 + 0.1\left(1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots\right) \quad (173)$$

where $x < 1 + x_1$, x_1 being the value of x corresponding to y_1. The entire integral curve passing through (0, 1.1) could be calculated by a series of such steps.

In actual practice, the Picard method would never be used to deal with such a simple equation as (163) where the variables are immediately separable. When the process is applied to more complex equations, the succeeding integrations become difficult if not impossible to perform.

Convenient methods of handling such cases are either to fit $f(x,y)$ by an interpolation formula (Chap. VII), which can be

integrated, or to integrate with an approximate formula such as Simpson's rule. One of the simplest and best methods of this type is that of W. E. Milne.

62. Method of W. E. Milne.* Consider again the general equation

$$\frac{dy}{dx} = f(x,y) \equiv f \tag{174}$$

and let it be specified that the integral curve shall pass through x_0, y_0. The first four points on the integral curve must be calculated by the modified Euler method, the Runge-Kutta method (see below), or the power-series method. The subsequent values of y are then obtained as follows:

$$(a) \qquad y_n^{(1)} = y_{n-4} + \frac{4\Delta x}{3}(2f_{n-1} - f_{n-2} + 2f_{n-3}) \tag{175}$$

(*b*) This value of $y_n^{(1)}$ is substituted into (174), together with x_n, to obtain the corresponding value of f_n.

(*c*) The resulting value of f_n is now substituted into the formula

$$y_n^{(2)} = y_{n-2} + \frac{\Delta x}{3}(f_n + 4f_{n-1} + f_{n-2}) \tag{176}$$

If these two successive values of y_n agree to the desired number of significant figures, $y_n^{(2)}$ is taken to be the correct value of y_n and is substituted in (174) along with x_n to obtain the correct value of f_n. The process is now repeated for the next interval.

On the other hand, if $y_n^{(1)}$ and $y_n^{(2)}$ do not agree, we may compute the error E due to approximate integration by formula (176).

$$E = \frac{y_n^{(2)} - y_n^{(1)}}{29} \tag{177}$$

If this error is not large enough to affect the last significant figure we desire to retain in y_n, $y_n^{(2)}$ may be accepted and the process repeated for another interval. Otherwise, the only recourse is to repeat the entire calculation using a smaller value of the interval Δx.

Although it is not necessary to be familiar with the detailed derivation of formulas (175) and (176) in order to use them successfully, it may be stated that both arise from approximating

* *Am. Math. Monthly*, **33**, 455 (1926); see also J. B. Scarborough, "Numerical Mathematical Analysis," Johns Hopkins Press, Baltimore, 1930.

$f(x,y)$ by Newton's interpolation formulas neglecting differences of the fourth order (see Chap. VII). Formula (176) turns out to be nothing but Simpson's rule applied over the interval $(n-2)$, n.

To illustrate systematic application of the method, we shall solve the following nonlinear equation of the first order:

$$\frac{dy}{dx} = x + 0.1y^2 \tag{178}$$

The solution of (178) cannot be obtained by any of the exact analytical methods discussed in the first part of the chapter and cannot be expressed in terms of a finite number of elementary functions. If an integral curve is to be obtained, it must be obtained by an approximate method. Let it be specified that the integral curve pass through the point $x = 1.8$, $y = 0$. The first four points on the curve are calculated by the modified Euler method, the values being tabulated in Table VII. The first point, *i.e.*, $x = 1.8$, $y = 0$, is designated point 0. The column headed 1 considers the interval between point 0 and point (1). As before, subscripts a and b refer to values of quantities at the beginning and end of an interval. The value

TABLE VII

	1	2	3	4	5	6	7	8
x_a	1.80	2.00	2.20	2.40	2.60	2.80	3.00	3.20
y_a	0.00	0.38	0.81	1.29	1.84	2.47	3.21	4.10
Δx	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
$\left(\frac{dy}{dx}\right)_a$	1.80	2.01	2.27	2.57	2.94	3.41	4.04	4.89
$\left(\frac{dy}{dx}\right)_a \cdot \Delta x$	0.36	0.40	0.45	0.51				
$y_b^{(1)}$	0.36	0.78	1.26	1.80	2.47	3.22	4.10	5.19
$\left(\frac{dy}{dx}\right)_b^{(1)}$	2.01	2.26	2.56	2.92				
$\left(\frac{dy}{dx}\right)_{av}^{(1)}$	1.91	2.13	2.41	2.75				
$\left(\frac{dy}{dx}\right)_{av}^{(1)} \cdot \Delta x$	0.38	0.43	0.48	0.55				
$y_b^{(2)}$	0.38	0.81	1.29	1.84	2.47	3.21	4.10	5.19
$\left(\frac{dy}{dx}\right)_b^{(2)}$	2.01	2.27	2.57	2.94	3.41	4.04	4.89	6.09

TABLE VIII

$$y_4^{(1)} = 0 + \frac{0.8}{3}[2(2.57) - 2.27 + 2(2.02)] = 1.84;$$

$$\frac{dy}{dx} = 2.60 + 0.1(1.84)^2 = 2.94$$

$$y_4^{(2)} = 0.81 + \frac{0.20}{3}[2.94 + 4(2.57) + 2.27] = 1.84$$

$$\frac{dy}{dx} = 2.60 + 0.1(1.84)^2 = 2.94$$

$$E = \frac{1.84 - 1.84}{29} = \frac{0}{29} = 0$$

Since this error does not affect the second decimal place, we may proceed to the next point.

$$y_5^{(1)} = 0.38 + \frac{0.8}{3}[2(2.94) - 2.57 + 2(2.27)] = 2.47;$$

$$\frac{dy}{dx} = 2.80 + 0.1(2.47)^2 = 3.40$$

$$y_5^{(2)} = 1.29 + \frac{0.20}{3}[3.40 + 4(2.94) + 2.57] = 2.47;$$

$$\frac{dy}{dx} = 2.80 + 0.1(2.47)^2 = 3.41$$

$$y_6^{(1)} = 0.81 + \frac{0.8}{3}[2(3.41) - 2.94 + 2(2.57)] = 3.22;$$

$$\frac{dy}{dx} = 3.00 + 0.1(3.22)^2 = 4.04$$

$$y_6^{(2)} = 1.84 + \frac{0.2}{3}[4.04 + 4(3.41) + 2.94] = 3.22;$$

$$\frac{dy}{dx} = 3.00 + 0.1(3.22)^2 = 4.04$$

$$y_7^{(1)} = 1.29 + \frac{0.8}{3}[2(4.04) - 3.41 + 2(2.94)] = 4.11;$$

$$\frac{dy}{dx} = 3.20 + 0.1(4.11)^2 = 4.89$$

$$y_7^{(2)} = 2.47 + \frac{0.2}{3}[4.89 + 4(4.04) + 3.41] = 4.10;$$

$$\frac{dy}{dx} = 3.20 + 0.1(4.10)^2 = 4.88$$

$$y_8^{(1)} = 1.84 + \frac{0.8}{3}[2(4.88) - 4.04 + 2(3.41)] = 5.19;$$

$$\frac{dy}{dx} = 3.41 + 0.1(5.19)^2 = 6.09$$

$$y_8^{(2)} = 3.22 + \frac{0.2}{3}[6.09 + 4(4.88) + 4.04] = 5.19$$

of y at the end of the fourth interval, *i.e.*, y_4, is calculated by the Euler and the Milne methods. Both methods agree indicating that the first five points are correct to the accuracy of the present calculation. Note that for the calculation of $y_5^{(1)}$ by the Milne

method, y_{n-4} refers to y at point 0. Successive values of y are calculated by the Milne method. Over the range of calculation ($x = 1.8$ to 3.4), an increment of 0.2 in x suffices to give accuracy to two decimal places. When the points thus calculated are plotted on Fig. 38, they fall directly on the integral curve calculated by a graphical method to be described in a following paragraph.

63. Method of Runge-Kutta. A rather different method of procedure has been described by Runge* and elaborated by Kutta.† In this method, formulas are derived that enable the direct calculation of the increment in y corresponding to an increment in x. In application to the problem of calculating an integral curve of the equation $dy/dx = f(x,y)$ through the point x_0, y_0, these formulas are

$$k_1 = f(x_0,y_0)\Delta x \tag{179}$$

$$k_2 = f\left(x_0 + \frac{\Delta x}{2}, y_0 + \frac{k_1}{2}\right)\Delta x \tag{180}$$

$$k_3 = f\left(x_0 + \frac{\Delta x}{2}, y_0 + \frac{k_2}{2}\right)\Delta x \tag{181}$$

$$k_4 = f(x_0 + \Delta x, y_0 + k_3)\Delta x \tag{182}$$

$$\Delta y = \tfrac{1}{6}(k_1 + 2k_2 + 2k_3 + k_4) \tag{183}$$

$$x_1 = x_0 + \Delta x \tag{184}$$

$$y_1 = y_0 + \Delta y \tag{185}$$

To compute a second point on the integral curve, the same set of formulas may be applied in the order given, x_0 and y_0 being replaced by x_1 and y_1. The derivation of this set of equations is involved and will not be given here. The error in this method is not easy to estimate, but it is known to be of the same order as that in Simpson's rule; and it is of interest to note that when $dy/dx = f(x)$ the method reduces to Simpson's rule.

For illustration, consider again the equation

$$\frac{dy}{dx} = x + 0.1y^2$$

The particular integral curve we are seeking is to pass through the point ($x = 1.8, y = 0$). The x increment will be taken as

* RUNGE, C., *Math. Ann.*, Vol. 46 (1895).

† KUTTA, W., *Z. Math. Phys.*, Vol. 46 (1901). See also Scarborough, *loc. cit.*

TABLE IX

	$x_0 = 1.8,\ y_0 = 0$	$x_1 = 2.10,\ y_1 = 0.59$
Δx	0.30	0.30
k_1	$(1.80 + 0)(0.30) = 0.54$	$[2.10 + 0.1(0.59)^2]0.30 = 0.64$
k_2	$\left[1.80 + \frac{0.30}{2} + 0.1\left(0 + \frac{0.54}{2}\right)^2\right]0.30 = 0.58$	$\left[2.10 + \frac{0.30}{2} + 0.1\left(0.59 + \frac{0.64}{2}\right)^2\right]0.30 = 0.70$
k_3	$\left[1.80 + \frac{0.30}{2} + 0.1\left(0 + \frac{0.58}{2}\right)^2\right]0.30 = 0.59$	$\left[2.10 + \frac{0.30}{2} + 0.1\left(0.59 + \frac{0.70}{2}\right)^2\right]0.30 = 0.70$
k_4	$[1.80 + 0.30 + 0.1(0 + 0.59)^2]0.30 = 0.64$	$[2.10 + 0.30 + 0.1(0.59 + 0.7)^2]0.30 = 0.77$
Δy	$\frac{1}{6}[0.54 + 2(0.58) + 2(0.59) + 0.64] = 0.59$	$\frac{1}{6}[0.64 + 2(0.70) + 2(0.70) + 0.77] = 0.70$
	$x_2 = 2.40,\ y_2 = 1.29$	$x_3 = 2.70,\ y_3 = 2.15$
Δx	0.30	0.30
k_1	$[2.40 + 0.1(1.29)^2](0.30) = 0.77$	$[2.70 + 0.1(2.15)^2](0.3) = 0.95$
k_2	$\left[2.40 + \frac{0.30}{2} + 0.1\left(1.29 + \frac{0.77}{2}\right)^2\right]0.30 = 0.85$	$\left[2.70 + \frac{0.30}{2} + 0.1\left(2.15 + \frac{0.95}{2}\right)^2\right]0.30 = 1.06$
k_3	$\left[2.40 + \frac{0.30}{2} + 0.1\left(1.29 + \frac{0.85}{2}\right)^2\right]0.30 = 0.86$	$\left[2.70 + \frac{0.30}{2} + 0.1\left(2.15 + \frac{1.06}{2}\right)^2\right]0.30 = 1.06$
k_4	$[2.40 + 0.30 + 0.1(1.29 + 0.86)^2]0.30 = 0.95$	$[2.70 + 0.30 + 0.1(2.15 + 1.06)^2]0.30 = 1.21$
Δy	$\frac{1}{6}[0.77 + 2(0.85) + 2(0.86) + 0.95] = 0.86$	$\frac{1}{6}[0.95 + 2(1.06) + 2(1.06) + 1.21] = 1.07$
	$x_4 = 3.00,\ y_4 = 3.22$	$x_5 = 3.30,\ y_4 = 4.62$
Δx	0.30	0.30
k_1	$[3.00 + 0.1(3.22)^2]0.30 = 1.21$	$[3.30 + 0.1(4.62)^2]0.30 = 1.63$
k_2	$\left[3.00 + \frac{0.30}{2} + 0.1\left(3.22 + \frac{1.21}{2}\right)^2\right]0.30 = 1.39$	$\left[3.30 + \frac{0.30}{2} + 0.1\left(4.62 + \frac{1.63}{2}\right)^2\right]0.30 = 1.92$
k_3	$\left[3.00 + \frac{0.30}{2} + 0.1\left(3.22 + \frac{1.39}{2}\right)^2\right]0.30 = 1.41$	$\left[3.30 + \frac{0.30}{2} + 0.1\left(4.62 + \frac{1.92}{2}\right)^2\right]0.30 = 1.97$
k_4	$[3.00 + 0.30 + 0.1(3.22 + 1.41)^2]0.30 = 1.63$	$[3.30 + 0.30 + 0.1(4.62 + 1.97)^2]0.30 = 2.38$
Δy	$\frac{1}{6}[1.21 + 2(1.39) + 2(1.41) + 1.63] = 1.40$	$\frac{1}{6}[1.63 + 2(1.92) + 2(1.97) + 2.38] = 1.96$

0.3. A systematic tabulation of the calculation appears in Table IX.

If the points resulting from this calculation are plotted on Fig. 38, they coincide with the integral curve there obtained by the graphical method. The value of $y = 3.22$ at $x = 3.00$ may be compared with the value of 3.21 given in Table VII.

64. Graphical Solution of Differential Equations. The integrations necessarily accompanying solution of a differential equation by the method of successive approximations may often be carried out more conveniently graphically than by the numerical methods previously described. Each successive approximation to a point on the integral curve given by Eqs. (159), (160), etc., is determined by graphical evaluation of the integrals in these equations according to either of the two methods described in Pars. 3 and 4.

As an illustration of this graphical procedure, let us consider an extension of a problem in distillation discussed in Par. 25. It will be recalled that the case considered was simplified by the assumption that the vapors rising from plate I were thoroughly mixed before they entered plate II. In the present problem, it will be assumed that the vapors evolved from plate I undergo no mixing as they rise to enter plate II. The apparatus will continue to operate at total reflux, and the vapor evolved by the still will have a composition of 10 mol per cent A. It is required to calculate the composition of the liquid returning from the condenser to plate II. By a material balance, the liquid returning to the still will be 10 mol per cent A, and the composition of liquid on plate I is given as a function of l/L by the integration of Eq. (41) between the limits of $x_1 = x_1$, $l/L = l/L$, and $x_1 = 0.1$, $l/L = 1$.

This equation, obtained from (42) by replacing Y_1 by x_1 and 1 (on the right-hand side) by l/L, is

$$\frac{2.00}{(1.90)^2} \ln \frac{1.90x_1 - 0.1}{0.09} + \frac{x_1 - 0.10}{1.90} = \frac{l}{L} \qquad (186)$$

y_1^*, the composition of vapor in equilibrium with x_1 is calculated from Eq. (40) (Par. 25) $y_1^* = \dfrac{2x_1}{1 + x_1}$. Both x_1 and y_1^* are plotted as functions of l/L in Fig. 37. Thus far, the procedure is not essentially different from that in the previous problem.

However, when we attempt to integrate the material balance

$$\frac{dl}{L}(y_2^* - y_1^*) = -\frac{O}{V}dx_2 \tag{187}$$

across plate II, complications are encountered due to the fact that y_1^* is not now constant but is a function of $l\ L$ given by Eq. (186) and the equilibrium relation between y_1^* and x_1. Equation (187) may be rearranged to the standard first-order form

$$\frac{dx_2}{d(l/L)} = -\left(\frac{2x_2}{1 + x_2}\right) + f\left(\frac{l}{L}\right) \tag{188}$$

$f(l\ L)$ denoting the value of y_1^* from the equilibrium relation in terms of x_1 from (186). Equation (188) cannot be solved analytically.

Inasmuch as the relation between x_1 on plate I and l/L is identical with the case considered in Par. 25, it is apparent that the liquid flowing from plate II to plate I must have the composition found in this previous case, $x = 0.294$. Therefore, the integral curve for x_2 must pass through the point $x_2 = 0.294$, $l/L = 1$, corresponding to conditions at the extreme right of plate II. In order to calculate the integral curve across the plate, it will be necessary to proceed from this point to the left through decreasing values of $l\ L$. We first assume that over a suitably small interval $\Delta(l\ L)$, $dx_2\ [d(l\ L)]$ is constant at its value at $x_2 = 0.294$ at $l\ L = 1$. Starting at this point on Fig. 37, we draw a line of slope $dx_2\ [d(l\ L)]$ to point A corresponding to an interval $\Delta(l\ L) = 0.1$. From this line and (40) it is possible to calculate the curve of y_2^* vs. $l\ L$ over this same interval. It is now possible to improve this first approximation to the integral curve over this interval by integration of (187)

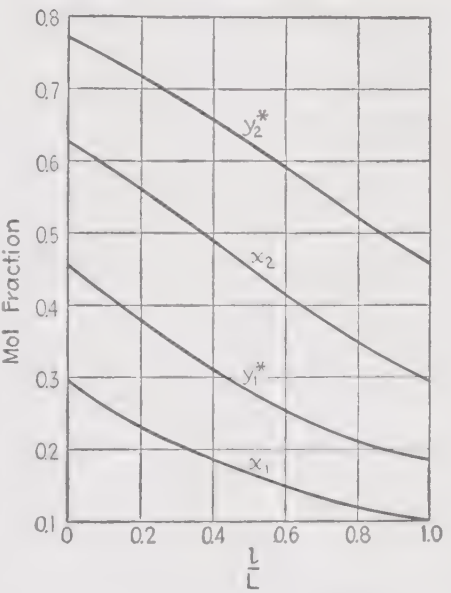

FIG. 37.—Solution of problem of rectifying column with cross down pipes.

$$\int_1^{\frac{l}{L}} (y_2^* - y_1^*)\frac{dl}{L} = -\int_{0.294}^{x_2} dx_2 = 0.294 - x_2 \qquad (189)$$

Having y_2^* as a function of l/L in Fig. 37, the integral on the left in (189) may be evaluated graphically as the area bounded by the (l/L) axis, the ordinates at $l/L = 1$ and $l/L = l/L$, and the curve of $y_2^* - y_1^*$ vs. l/L. By this means, a second approximation to the curve of x_2 vs. l/L is obtained. A second approximation to the curve of y_2 vs. l/L is now calculated from the equilibrium relation, and this curve may be employed to obtain a third approximation by repetition of the foregoing procedure. The curve over the next interval is established by the same procedure. If the integral curve is calculated to the point $l/L = 0$ as shown in Fig. 37, it is found that $x_2 = 0.626$. This must be the composition of the liquid returning from the condenser.

65. Graphical Solution by the Picard Process. The Picard process may be carried out graphically as well as analytically, and by a proper selection of coordinate axes the successive approximations may be made to converge to the correct value quite rapidly.* To illustrate this graphical method of solution, we shall again determine the integral curve of the equation $dy/dx = x + 0.1y^2$ through the point $x = 1.8$, $y = 0$.

If $x + 0.1y^2$ is placed equal to a constant C, the resulting curve will be the locus of all the points in the plane where the slope of an integral curve is $dy/dx = C$. These loci of constant slope are known as "isoclinals"; the isoclinals in this case are parabolas with their axes coincident with the x axis. Only those portions of the isoclinals actually used in the calculation have been shown in Fig. 38. Associated with each isoclinal having the equation $f(x,y) = C$, there is a definite direction in the plane, which may be indicated by a line crossing the x axis at an angle of $\tan^{-1} C$. The directions associated with the isoclinals may be conveniently represented by a group of rays emerging from a common origin R. The ray R-1 having a slope of 1 is associated with the parabola $f(x,y) = 1$, for all integral curves having points in common with this parabola

* See SANDEN, H. VON, "Practical Mathematical Analysis," E. P. Dutton & Co., Inc., New York, 1913.

have a slope of 1 at these points. Similar relations exist between the other rays and their corresponding parabolas.

The problem of determining the integral curve through the point ($x = 1.8, y = 0$) may now be visualized from a graphical standpoint. Construction of the integral curve consists in drawing a curve through the point (1.8,0), the direction of this

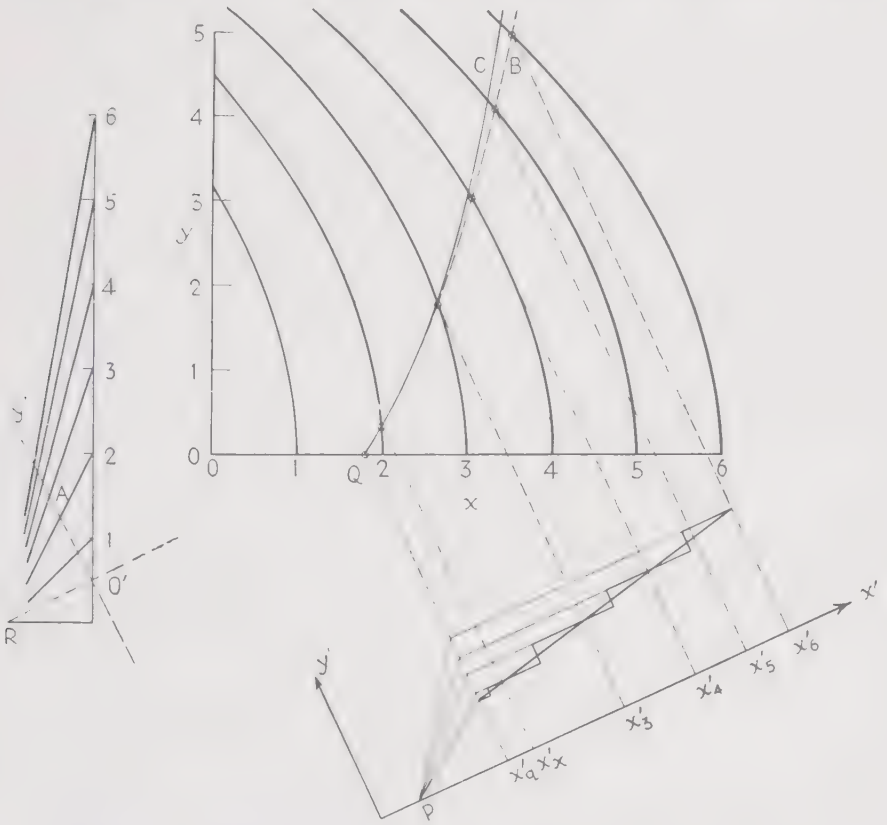

FIG. 38.—Graphical solution of differential equation by Picard method.

curve as it crosses any isoclinal being parallel to the ray associated with this isoclinal. As a first approximation to the desired integral curve, the dotted line QB was sketched in from these considerations. It is essential to realize that once the relative directions of the isoclinals and the group of associated rays have been established, given the starting point Q, this integral curve may be constructed entirely independently of any reference coordinate axes, the direction of the integral curve at its point of intersection with an isoclinal being completely

determined by the corresponding rays. It is possible to take advantage of this fact to effect a rapid convergence of the process of successive approximation to the true integral curve.

Let us take a new set of coordinates x', y' and locate the coordinate axes so that the x' axis is as nearly as possible perpendicular to the direction of the isoclinals at their points of intersection with the integral curve. With reference to the new axes, the differential Eq. (178) may be written

$$\frac{dy'}{dx'} = \psi(x',y') \tag{190}$$

and the solution will be

$$y' = y'_0 + \int_{x'_0}^{x'} \psi(x',y')dx'$$

The function $\psi(x',y')$, which is the equation of the isoclinals relative to the x', y' axis, plays a part in this new coordinate system exactly analogous to the part played by $f(x,y)$ in the x-y system. The point y'_0, x'_0 is definitely known as the point Q on the diagram, and it remains to evaluate

$$\int_{x'_0}^{x'} \psi(x',y')dx',$$

y' being the value of y from the first approximation denoted in the previous numerical methods as $y^{(1)}$. This integral may be evaluated graphically by the procedure described in Par. 4 if a graph is made of $\psi(x',y')$ vs. x'. At the point of intersection of each isoclinal with the first approximate integral curve, a perpendicular is dropped to the x' axis (dotted lines in Fig. 38). A value of $\psi(x',y')$ corresponding to the value of x' determined by the intersection of each perpendicular with the x' axis may now be obtained from the group of rays by a simple graphical construction. Through point R, the common origin of all the rays, we draw a line parallel to the x' axis, and, through any convenient point O' on this line, draw a line parallel to the y' axis long enough to intersect all of the rays. Clearly, the distance along this line from O' to the point where any ray crosses, measured in terms of $O'R$ as a unit, is the slope of this ray relative to the x', y' axes. Since point Q is on the isoclinal passing through $f(x,y) = 1.8$, we erect an ordinate on the x' axis at x'_q equal to the distance from O' along $O'Y'$ to the intersection of the ray having a slope of 1.8 relative to the x-y

axis. This ordinate represents the value of $f(x',y')$ at x'_q. Similarly, at x'_3 corresponding to the intersection of the approximate integral curve with the isoclinal $f(x,y) = 3.0$, an ordinate equal in length to $O'A$ is erected. The other ordinates at x'_2, x'_4, x'_5 and x'_6 are obtained by a similar procedure. The resulting points are connected by a smooth curve, which may be integrated directly by the procedure of Par. 4 if the distance $O'R$ is laid off from x'_q to P as the polar distance. The resulting integral curve QC is very near and similar in shape to the more approximate dotted curve. Owing to the location of the x axis in a position almost perpendicular to the direction of the isoclinals at the points of intersection with the integral curves, the abscissas on the x' axis of the intersections of the first two approximations to the integral curve are so nearly coincident that another repetition of the Picard approximation process would result in a curve practically coincident with QC within the limits of the widths of the lines on the diagram.

Once the isoclinals have been plotted, solution by this graphical method proceeds very rapidly. If, however, $f(x,y)$ is such a complicated relationship as to make the isoclinals difficult to plot, the method may become too time-consuming for practical use. As a simplification of the process, it is sometimes convenient to omit both isoclinals and rays, obtaining the ordinates at x'_q, x'_2, etc., by computation from (190). This is convenient only when (190) is easily obtained from the original differential equation.

66. Numerical Solution of Equations of Higher Order. Any equation of higher order may be reduced to a set of first-order equations by the introduction of auxiliary variables. For example, the second-order equation

$$\frac{d^2y}{dx^2} + y^2\frac{dy}{dx} + y = 0 \tag{191}$$

may be reduced to a set of first-order equations by placing $dy/dx = z$, whereupon $d^2y/dx^2 = dz/dx$, and (191) becomes equivalent to two equations.

$$\frac{dz}{dx} + y^2z + y = 0 \tag{192}$$

$$\frac{dy}{dx} = z \tag{193}$$

These two first-order simultaneous equations may be solved by any of the previous methods. In order to illustrate the method of attack, we shall first solve a simple second-order equation. Let us calculate the integral curve of

$$\frac{d^2y}{dx^2} - y = 0 \tag{194}$$

passing through the point $x = 0$, $y = 1.00$ and having $dy/dx = 0$ at this point. Notice that to calculate an integral curve of this second-order equation it is necessary to specify two conditions corresponding to an assignment of values to the two arbitrary constants that must occur in its general solution. The necessity for these two conditions is emphasized as soon as we replace (194) by its equivalent set of first-order equations

$$\frac{dz}{dx} = y \tag{195}$$

$$\frac{dy}{dx} = z \tag{196}$$

These equations will be used to calculate curves of y vs. x and of z vs. x, but, before it is possible to start either of the two curves, initial values of y and $z = dy/dx$ must be selected at a given value of x. Starting at $x = 0$, $y = 1.000$, and $z = 0$ (Fig. 39), we assume that dz/dx is constant over the short interval from $x = 0$ to $x = 0.050$. At $x = 0.050$,

$$z_1^{(1)} = z_0 + \left(\frac{dz}{dx}\right)\Delta x = 0.00 + 1(0.050) = 0.050.$$

Using the arithmetic average value of z over the interval, we compute

$$z_{av} = \frac{(z_0 + z_1^{(1)})}{2} = \left(\frac{dy}{dx}\right)_{av}$$

$$y_b^{(1)} = y_a + \left(\frac{dy}{dx}\right)_{av} \cdot \Delta x = 1.000 + 0.001 = 1.001.$$

In a similar manner, second approximations to y_1 and z_1 are computed by employing new arithmetic average values of dy/dx and dz/dx over the interval based on $z_1^{(2)}$ and $y_1^{(2)}$.

To continue the two curves, we pass to the points x_1, y_1 and z_1, take a new increment in x equal to 0.050, and repeat the

TABLE X

Interval	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
x_a	0	0.050	0.100	0.150	0.200	0.250	0.300	0.350	0.400	0.450	0.500	0.550	0.600	0.650	0.700	0.750	0.800	0.850
Δx	0.050	0.050	0.050	0.050	0.050	0.050	0.050	0.050	0.050	0.050	0.050	0.050	0.050	0.050	0.050	0.050	0.050	0.050
x_b	0.050	0.100	0.150	0.200	0.250	0.300	0.350	0.400	0.450	0.500	0.550	0.600	0.650	0.700	0.750	0.800	0.850	0.900
$y_a = \left(\frac{dz}{dx}\right)_a$	1.000	1.001	1.004	1.010	1.018	1.030	1.044	1.060	1.079	1.101	1.125	1.152	1.182	1.215	1.251	1.290	1.332	1.378
$\frac{dz}{dx}\Delta x = \Delta z$	0.050	0.050	0.050	0.050	0.051	0.051	0.052	0.053	0.054	0.055	0.056	0.058	0.059	0.061	0.063	0.065	0.067	0.069
z_a	0.000	0.050	0.100	0.150	0.200	0.251	0.302	0.354	0.407	0.461	0.516	0.572	0.630	0.689	0.750	0.813	0.878	0.945
$z_b^{(1)}$	0.050	0.100	0.150	0.200	0.251	0.302	0.354	0.407	0.461	0.516	0.572	0.630	0.689	0.750	0.813	0.878	0.945	1.014
$z_{av}^{(1)} = \frac{z_a + z_b^{(1)}}{2} = \left(\frac{dy}{dx}\right)_{av}^{(1)}$	0.025	0.075	0.120	0.170	0.225	0.276	0.328	0.380	0.434	0.488	0.544	0.600	0.659	0.717	0.781	0.845	0.911	0.979
$\left(\frac{dy}{dx}\right)_{av}^{(1)}\Delta x = \Delta y$	0.001	0.003	0.006	0.009	0.012	0.014	0.016	0.019	0.022	0.024	0.027	0.030	0.033	0.036	0.039	0.042	0.045	0.049
$y_b^{(1)}$	1.001	1.004	1.010	1.018	1.030	1.044	1.060	1.079	1.101	1.125	1.152	1.182	1.215	1.251	1.290	1.332	1.377	1.427
$y_{av} = \frac{y_a + y_b^{(1)}}{2} = \left(\frac{dz}{dx}\right)_{av}^{(1)}$	1.000	1.003	1.007	1.014	1.024	1.037	1.052	1.069	1.090	1.113	1.138	1.167	1.198	1.233	1.270	1.311	1.354	1.402
$\left(\frac{dz}{dx}\right)_{av}^{(1)}\Delta x = \Delta z$	0.050	0.050	0.050	0.051	0.052	0.053	0.054	0.055	0.056	0.057	0.058	0.060	0.060	0.062	0.064	0.066	0.068	0.070
$z_b^{(2)}$	0.050	0.050	0.150	0.201	0.251	0.303	0.355	0.407	0.461	0.517	0.573	0.630	0.690	0.751	0.814	0.878	0.946	1.015
$z_{av}^{(2)} = \frac{z_a + z_b^{(2)}}{2} = \left(\frac{dy}{dx}\right)_{av}^{(2)}$	0.025	0.075	0.100	0.170	0.225	0.277	0.328	0.380	0.434	0.489	0.544	0.601	0.660	0.720	0.782	0.845	0.912	0.980
$\left(\frac{dy}{dx}\right)_{av}^{(2)} \cdot \Delta x = \Delta y$	0.001	0.003	0.005	0.008	0.012	0.014	0.016	0.019	0.022	0.024	0.027	0.030	0.033	0.036	0.039	0.042	0.046	0.049
$y_b^{(2)}$	1.001	1.004	1.010	1.018	1.030	1.044	1.060	1.079	1.101	1.125	1.152	1.182	1.215	1.251	1.290	1.332	1.378	1.427

foregoing process. If a calculation of this nature is to be successful, it should be organized into a table. This has been done in Table X, where subscripts a and b indicate values at the beginning and end of an interval. The exact solution of (194) as obtained by the methods of Par. 51 is

$$y = C_1 e^x + C_2 e^{-x} \tag{197}$$

When $x = 0$, $y = 1$, and $C_1 + C_2 = 1$.
Differentiating (197) gives, at $x = 0$,

$$\frac{dy}{dx} = C_1 - C_2 = 0$$

Therefore, $C_1 = C_2 = \frac{1}{2}$ and

$$y = \frac{e^x + e^{-x}}{2} = \cosh x$$

$$\frac{dy}{dx} = z = \sinh x$$

The accuracy of the numerical method as employed in the present case may be judged from the fact that curves of $y = \cosh x$

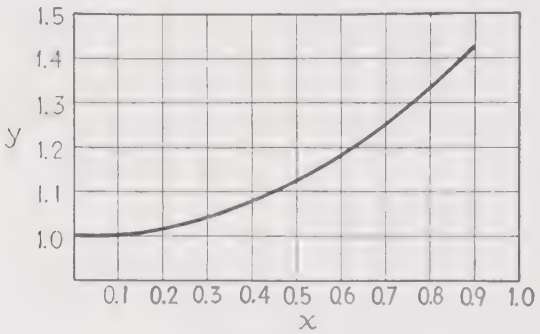

FIG. 39.

and $z = \sinh x$ may be superimposed on the curves of Figs. 39 and 40.

It would be entirely possible to carry out this calculation graphically, increments of the two curves being drawn in with the proper slopes, by a process of approximation. There is usually no advantage to the graphical method, and the numerical procedure is more accurate.

67. Extension of the Method of Runge-Kutta to Equations of Higher Order. To integrate numerically an equation of higher

order by this method, we first obtain the equivalent system of first-order equations and compute increments by means of a set

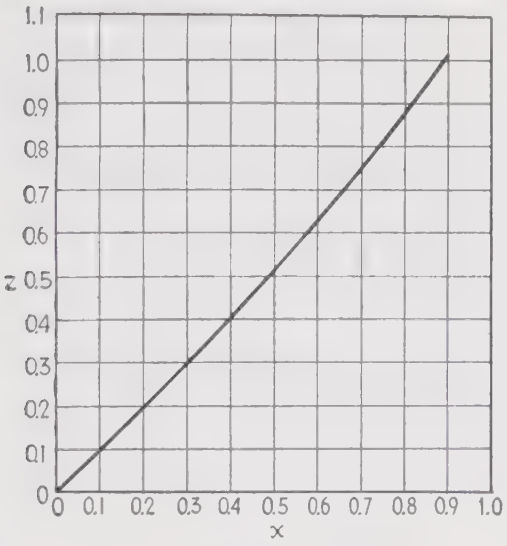

FIG. 40.

of formulas similar to those used for a single equation (Par. 63). Consider the simultaneous equations

$$\frac{dz}{dx} = f_1(x,y,z)$$
$$\frac{dy}{dx} = f_2(x,y,z)$$

Starting at x_0, y_0, z_0, the increments in y and z for the first increment in x are computed by means of the formulas

$$k_1 = f_1(x_0,y_0,z_0)\Delta x \tag{198}$$

$$k_2 = f_1\left(x_0 + \frac{\Delta x}{2}, y_0 + \frac{k_1}{2}, z_0 + \frac{l_1}{2}\right)\Delta x \tag{199}$$

$$k_3 = f_1\left(x_0 + \frac{\Delta x}{2}, y_0 + \frac{k_2}{2}, z_0 + \frac{l_2}{2}\right)\Delta x \tag{200}$$

$$k_4 = f_1(x_0 + \Delta x, y_0 + k_3, z_0 + l_3)\Delta x \tag{201}$$

$$\Delta y = \tfrac{1}{6}(k_1 + 2k_2 + 2k_3 + k_4) \tag{202}$$

$$l_1 = f_2(x_0,y_0,z_0)\Delta x \tag{203}$$

$$l_2 = f_2\left(x_0 + \frac{\Delta x}{2}, y_0 + \frac{k_1}{2}, z_0 + \frac{l_1}{2}\right)\Delta x \tag{204}$$

$$l_3 = f_2\left(x_0 + \frac{\Delta x}{2}, y_0 + \frac{k_2}{2}, z_0 + \frac{l_2}{2}\right)\Delta x \tag{205}$$

$$l_4 = f_2(x_0 + \Delta x, y_0 + k_3, z_0 + l_3)\Delta x \tag{206}$$

$$\Delta z = \tfrac{1}{6}(l_1 + 2l_2 + 2l_3 + l_4) \tag{207}$$

To compute the next increment, it is necessary only to replace x_0, y_0, and z_0 in these formulas by x_1, y_1, and z_1. Extension of the method to four or more variables is effected by a set of equations analogous to those above.

68. Solution of Simultaneous Equations by the Milne Method. The Milne method is applicable to simultaneous equations, and hence to equations of higher order, with no changes in the formulas already given. This method will be applied to obtain a solution of the three simultaneous equations developed by the air-water interaction process (Par. 35). The equations to be solved are

$$Ka(H_W - H)dh = W\,dH \tag{208}$$

$$Ua(T - t)dh = WS\,dt \tag{209}$$

$$L\,dT = h_{fg}W\,dH + WS\,dt \tag{210}$$

These equations will be applied to the problem of calculating the height of cooling tower necessary to cool water from 90 to 75°F. The water rate L amounts to 3,000 lb. per hr. per sq. ft. of tower cross section, and the dry air rate W is to be 2,000 lb. per hr. per sq. ft. The entering air has a temperature t of 70°F. and a humidity H of 0.0030. The tower will operate at 760 mm. Hg. Under these conditions, with the type of packing to be used, the heat-transfer coefficient Ua may be taken as 35.6 B.t.u. (hr.)(°F.)(cu. ft.), and the mass transfer coefficient Ka will be taken as constant at 105 lb. water (hr.)(unit of humidity difference)(cu. ft.). If sufficient data were available, it would be entirely possible to allow for variation in these two coefficients throughout the tower. The heat of vaporization of water h_{fg} will be considered constant at an average value of 1000 B.t.u. per lb., and the humid heat S will be taken constant at 0.26 B.t.u. per lb. per °F. Physically, it is clear that we have now specified a sufficient number of variables to fix the operation of this tower. The first step in the solution is to differentiate (210) and rearrange (208) and (209). This gives

$$\frac{dH}{dh} = \frac{Ka}{W}(H_W - H) \tag{211}$$

$$\frac{dt}{dh} = \frac{Ua}{WS}(T - t) \tag{212}$$

$$\frac{dT}{dh} = \frac{h_{fg}W\dfrac{dH}{dh} + WS\dfrac{dt}{dh}}{L} \tag{213}$$

One additional necessary relation is the vapor-pressure curve of water, from which it is possible to calculate H_w, the saturation humidity at the interface, as a function of T, the water temperature. These data are given in Table XI.

TABLE XI

T(°F.)	p (mm. Hg)	$H_w = \frac{18}{29}\left(\frac{p}{760 - p}\right)$
75.0	22.2	0.0188
76.8	23.6	0.0199
78.5	24.9	0.0210
80.1	26.2	0.0223
81.7	27.7	0.0237
83.0	29.0	0.0246
84.4	30.2	0.0258
85.8	31.6	0.0270
87.0	32.7	0.0279
88.2	34.0	0.0291
89.4	35.4	0.0304
90.6	36.8	0.0317

We now proceed to calculate the curves shown plotted in Fig. 41, H vs. h, t vs. h, and T vs. h. The first four points are calculated by the modified Euler method. At $H = 0.0030$, $(dH/dh)_a^{(1)}$ is calculated from (211) as 8.3×10^{-4} and assumed constant over an interval $\Delta h = 1$. $H_b^{(1)}$, the humidity at the end of this interval, is obtained as

$$H_b^{(1)} = H_a + \left(\frac{dH}{dh}\right)_a^{(1)} \Delta h = 0.0030 + 0.0008 = 0.0038$$

At $t = 70$, $(dt/dh)_a^{(1)}$ is calculated from (212) as 0.342, and this gives

$$t_b^{(1)} = t_a + (dt/dh)_a^{(1)}\Delta h = 70 + 0.34 = 70.3$$

We may now calculate $(dT/dh)_a^{(1)}$ as 0.61 and

$$T_b^{(1)} = 75 + 0.6 = 75.6$$

Calculation of a value of H_w at $T_b^{(1)}$ enables us to calculate $(dH/dh)_b^{(1)}$ at the end of this first interval. Using an arithmetic mean value of dH/dh at the beginning and end of the interval, a second approximation to H_b may be calculated. Second approximations prove to be sufficiently accurate for obtaining values in every case. The calculation is easily followed from Table XIII in columns $1a$, $2a$, $3a$, $4a$, where subscripts a and b indicate the values of quantities at the beginning and end of an interval, respectively. Superscripts denote first approximation, second approximation, etc. The subscript av on a derivative indicates its arithmetic average value at the beginning and end of an interval.

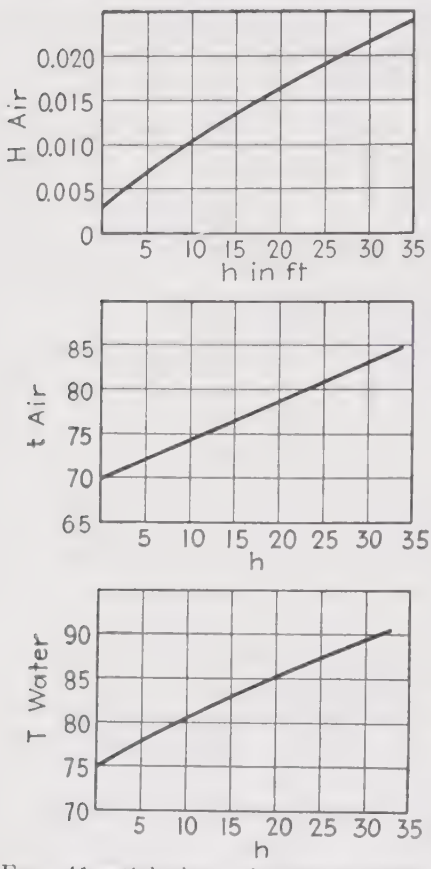

FIG. 41. Solution of cooling-tower problem.

The values converge so fast that it is expedient to enlarge the interval Δh from 1.0 to 3.0. This is done in the columns marked 1, 2, 3, and 4, where it may be seen that the convergence is still satisfactory. After four points have been obtained, the calculation is picked up by the Milne method. For convenience, the formulas for use with this method are repeated here. y represents any one of the dependent variables, H, t, or T; f represents the corresponding derivative with respect to h, *i.e.*, dH/dh, dt/dh, or dT/dh.

$$y_n^{(1)} = y_{n-4} + \frac{4\Delta h}{3}(2f_{n-1} - f_{n-2} + 2f_{n-3}) \tag{175}$$

$$y_n^{(2)} = y_{n-2} + \frac{\Delta h}{3}(f_n + 4f_{n-1} + f_{n-2}) \tag{176}$$

Formula (175) is now applied in succession to obtaining $H_4^{(1)}$, $t_4^{(1)}$, and $T_4^{(1)}$. When $T_4^{(1)}$ is obtained, a value for H_w at point 4

is acquired and it is possible to evaluate dH/dh at point 4. Formula (176) may now be applied successively to obtain $H_4^{(2)}$, $t_4^{(2)}$, and $T_4^{(2)}$. If these agree with the first approximations to the desired extent, we may proceed to the next point by means of repetition of the foregoing process. If $y_n^{(1)}$ and $y_n^{(2)}$ do not agree, we may compute the error E due to formula (176) by the equation $E = (y_n^{(2)} - y_n^{(1)})/29$. If this is large enough to affect the last significant figure we wish to retain, our only recourse is to repeat the whole calculation, using a smaller value of Δh. It is particularly important to note that the whole calculation must be repeated. The Milne method, being based upon an integration of Newton's interpolation formulas (Chap. VII) in terms of equal increments, will obviously not permit a change in the size of Δh in the middle of a calculation. As an example of the method of procedure, the calculations for intervals V and VI are given in detail in Table XII. Reference to formulas (175) and (176) and columns 1, 2, 3, and 4 of Table XIII will allow the source of each entry to be determined easily.

TABLE XII

Interval IV (Milne's Method)

$H_4^{(1)} = 0.0030 + 4[2(6.66) - 7.00 + 2(7.66)]10^{-4} = 0.0117$
$t_4^{(1)} = 70.0 + 4[2(0.445) - 0.425 + 2(0.390)] = 75.0$
$T_4^{(1)} = 75.0 + 4[2(0.52) - 0.54 + 2(0.576)] = 81.6$
H_w at $81.6 = 0.0237$
$(dH/dh)_4^{(1)} = 0.0525(0.0237 - 0.0117) = 6.3 \times 10^{-4}$
$H_4^{(2)} = 0.0077 + 1.00[6.3 + 4(6.66) + 7.00]10^{-4} = 0.0117$
$(dt/dh)_4 = 0.452$
$t_4^{(2)} = 72.3 + 1.00[0.452 + 4(0.445) + 0.425] = 75.0$
$(dT/dh)_4 = 0.498$
$T_4^{(2)} = 78.5 + 1.00[0.498 + 4(0.520) + 0.540] = 81.6$

Interval V

$H_5^{(1)} = 0.0055 + 4[2(6.3) - 6.66 + 2(7.00)]10^{-4} = 0.0135$
$t_5^{(1)} = 71.1 + 4[2(0.452) - 0.445 + 2(0.425)] = 76.3$
$T_5^{(1)} = 76.8 + 4[2(0.498) - 0.520 + 2(0.540)] = 83.0$
H_w at $83.0 = 0.0246$
$(dH/dh)_5^{(1)} = 0.0525(0.0246 - 0.0135) = 5.83 \times 10^{-4}$
$H_5^{(2)} = 0.0096 + 1.00[5.83 + 4(6.3) + 6.66]10^{-4} = 0.0134$
$(dt/dh)_5 = 0.459$
$t_5^{(2)} = 73.6 + 1.00[0.459 + 4(0.452) + 0.445] = 76.3$
$(dT/dh)_5 = 0.468$
$T_5^{(2)} = 80.1 + 1.00[0.468 + 4(0.498) + 0.520] = 83.1$

TABLE XIII

Interval	1a	2a	3a	4a	1	2	3	4
H_a	0.0030	0.0038	0.0046	0.0054	0.0030	0.0055	0.0077	0.0096
$(H_w)_a$	0.0188	0.0191	0.0195	0.0199	0.0188	0.0199	0.0210	0.0223
$\left(\frac{dH}{dh}\right)_a = \frac{Ka}{W}$								
$(H_w - H) \times 10^4$	8.30	8.04	7.84	7.61	8.3	7.66	7.00	6.66
Δh	1.00	1.00	1.00	1.00	3.00	3.00	3.00	3.00
$\left(\frac{dH}{dh}\right)_a \Delta h \times 10^4$	8.30	8.04	7.84	7.61	24.9	22.9	21.0	19.9
ΔH	0.00083	0.0008	0.0008	0.00076	0.0025	0.0023	0.0021	0.0020
$H_b^{(1)}$	0.00383	0.0046	0.0054	0.0062	0.0055	0.0078	0.0098	0.0116
T_a	75.0	75.6	76.2	76.8	75.0	76.8	78.5	80.1
t_a	70.0	70.4	70.7	71.1	70.0	71.1	72.3	73.6
$\left(\frac{dt}{dh}\right)_a = \frac{Ua}{WS}(T - t)$	0.342	0.356	0.377	0.390	0.342	0.390	0.425	0.445
$\left(\frac{dt}{dh}\right)_a \Delta h$	0.342	0.356	0.377	0.390	1.026	1.17	1.27	1.33
Δt	0.342	0.356	0.377	0.390	1.026	1.17	1.27	1.33
$t_b^{(1)}$	70.34	70.8	71.1	71.5	71.0	72.3	73.6	74.9
$h_{fg} W \left(\frac{dH}{dh}\right)_a$	1,660	1,600	1,568	1,522	1,660	1,532	1,400	1,332
$WS\left(\frac{dt}{dh}\right)_a$	178	185	196	203	178	203	220	232
$h_{fg} W \left(\frac{dH}{dh}\right)_a + WS\left(\frac{dt}{dh}\right)_a$	1,840	1,790	1,760	1,725	1,840	1,730	1,620	1,560
$\left(\frac{dT}{dh}\right)_a = \frac{h_{fg} W \left(\frac{dH}{dh}\right)_a + WS\left(\frac{dt}{dh}\right)_a}{L}$	0.61	0.597	0.584	0.575	0.61	0.576	0.540	0.520
$\left(\frac{dT}{dh}\right)_a \Delta h$	0.61	0.597	0.584	0.575	1.83	1.72	1.62	1.56
ΔT	0.61	0.597	0.584	0.575	1.83	1.72	1.62	1.56
$T_b^{(1)}$	75.6	76.2	76.8	77.4	76.8	78.5	80.1	81.7
$(H_w)_b^{(1)}$	0.0191	0.0194	0.0199	0.0203	0.0199	0.0210	0.0223	0.0237
$\left(\frac{dH}{dh}\right)_{av}^{(1)} \times 10^4$	8.37	7.91	7.72	7.50	7.66	7.30	6.78	6.50
$\left(\frac{dH}{dh}\right)_{av}^{(1)} \Delta h \times 10^4$	8.37	7.91	7.72	7.50	22.9	21.9	20.3	19.5
ΔH	0.00084	0.0008	0.00077	0.00075	0.0024	0.0022	0.0019	0.0019
$H_b^{(2)}$	0.0038	0.0046	0.0054	0.0062	0.0054	0.0077	0.0096	0.0115
$\left(\frac{dt}{dh}\right)_{av}^{(1)}$	0.350	0.363	0.383	0.397	0.365	0.407	0.435	0.452
$\left(\frac{dt}{dh}\right)_{av}^{(1)} \Delta h$	0.350	0.363	0.383	0.397	1.09	1.22	1.30	1.36
Δt	0.350	0.363	0.383	0.397	1.09	1.22	1.30	1.36
$t_b^{(2)}$	70.4	70.7	71.1	71.5	71.1	72.3	73.6	75.0
$\left(\frac{dT}{dh}\right)_{av}^{(1)}$	0.615	0.603	0.580	0.572	0.59	0.571	0.534	0.514
$\left(\frac{dT}{dh}\right)_{av}^{(1)} \Delta h$	0.615	0.603	0.580	0.572	1.77	1.71	1.60	1.50
ΔT	0.615	0.603	0.580	0.572	1.77	1.71	1.60	1.50
$T_b^{(2)}$	75.6	76.2	76.8	77.4	76.8	78.5	80.1	81.6
$(H_w)_b^{(2)}$	0.0191	0.0195	0.0199	0.0203	0.0199	0.0210	0.0223	0.0237

TABLE XIII.—(*Continued*)

	5*	6*	7*	8*	9*	10*	11*	12*
H_a	0.0117	0.0134	0.0152	0.0167	0.0184	0.0197	0.0213	0.0226
$(H_w)_a$	0.0237	0.0246	0.0258	0.0270	0.0279	0.0292	0.0304	0.0317
$\left(\frac{dH}{dh}\right)_a = \frac{Ka}{W}$								
$(H_w - H) \times 10^4$	6.30	5.80	5.56	5.35	5.06	4.88	4.72	4.67
Δh	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
$\left(\frac{dH}{dh}\right)_a \Delta h \times 10^4$								
ΔH								
$H_b^{(1)}$								
T_a	81.6	83.1	84.4	85.8	87.0	88.2	89.4	90.6
t_a	75.0	76.3	77.7	79.1	80.4	81.8	83.1	84.4
$\left(\frac{dt}{dh}\right)_a = \frac{Ua}{WS}(T - t)$	0.452	0.459	0.459	0.460	0.452	0.445	0.438	0.418
$\left(\frac{dt}{dh}\right)_a \Delta h$								
Δt								
$t_b^{(1)}$								
$h_{fg} W \left(\frac{dH}{dh}\right)_a$								
$WS\left(\frac{dt}{dh}\right)_a$								
$h_{fg} W \left(\frac{dH}{dh}\right)_a + WS\left(\frac{dt}{dh}\right)_a$								
$\left(\frac{dT}{dh}\right)_a =$								
$\frac{h_{fg} W \left(\frac{dH}{dh}\right)_a + WS\left(\frac{dt}{dh}\right)_a}{L}$	0.498	0.468	0.450	0.436	0.415	0.402	0.391	0.391

* Calculation by Milne method.

The results of similar calculations for succeeding intervals are tabulated in Table XIII. The calculation is stopped as soon as T reaches 90°F., the temperature at which the warm water enters the tower. The height of the tower, the sum of all the increments in h, is 32 ft.

69. General Remarks on Numerical Methods of Solution. Without question, an analytical solution to a differential equation is to be preferred to any of the numerical methods whenever it can be obtained, for the analytical solution will demonstrate the general behavior of the integral function, whereas the numerical methods furnish only one particular solution out of an infinite number. It is indeed unfortunate that comparatively few equations can be solved analytically, but there is some consolation in the fact that a numerical solution can be obtained for any ordinary differential equation. None of the methods

available for this task is difficult to apply in theory, but all of them are apt to give rise to tedious routine calculation in practice. These calculations, however, when organized into proper tables may be carried out by anyone equipped to perform the ordinary operations of arithmetic. The choice of a particular method to be selected in any case is somewhat arbitrary, but if the functions are at all complex it will be found that the method of Runge-Kutta involves more than the usual amount of labor. By means of the Milne method, one can ascertain whether he is within the limit of allowable error at every stage of the calculation, provided that the first four points are calculated correctly. With the other methods, the most practical means of estimating the error is a repetition of the entire calculation with the use of smaller increments.

CHAPTER IV

APPLICATIONS OF PARTIAL DIFFERENTIATION

70. Partial Differentiation. The methods of ordinary differentiation prove quite inadequate for the treatment of situations involving more than one independent variable, and the extension of the differential calculus to these cases constitutes the subject of partial differentiation. All of the familiar types of problems in one independent variable, requiring ordinary derivatives in their solution, are encountered in more generalized form involving several independent variables but now requiring partial derivatives in their solution.

The present chapter will develop the fundamental properties of partial differentials and derivatives and indicate several of their important applications, particularly in connection with the simplification of partial differential equations and in the field of applied chemical thermodynamics. Other applications of this subject are to be found throughout the book, notably in Chap. VI on partial differential equations, in Chap. V in connection with solution of ordinary differential equations by Taylor's series, in Chap. III in the section on exact equations, in the discussion of maximum and minimum values of functions of several variables in Chap. I, and in the theory of the propagation of errors described in Chap. IX.

71. Partial Derivatives of the First Order. The general function of n variables

$$w = f(x_1,x_2 \cdot \cdot \cdot x_n) \tag{1}$$

may be reduced to a function of x_1 alone by holding the remaining variables $x_2 \ldots x_n$ constant and allowing x_1 to vary. The function of x_1 thus created may have a derivative defined and computed by the ordinary methods applicable to functions of a single variable. This derivative is called the first partial derivative of f or w with respect to x_1, and its notation is the symbol f_{x_1} or $(df/dx_1)_{x_2 \cdots x_n}$ or $\partial f/\partial x_1$. In similar fashion, partial derivatives may be computed with respect to each of the

variables x_1, x_2 . . . x_n. Helpful geometric interpretations analogous to those characterizing the two partial derivatives of a function of two variables (Par. 8) do not exist in the case of functions of three or more variables which cannot be represented graphically, and partial differentiation in these cases can be thought of only as a formal mathematical operation.

Particular attention must be devoted to the notational aspects of partial differentiation, inasmuch as the customary symbols, carelessly employed, may become so nondescript with reference to the actual operations as to result in considerable ambiguity and confusion usually leading to a false result. The chief difficulty in this respect is with the common partial derivative symbol $(\partial f/\partial x_1)_{x_2 \ldots x_n}$.

The symbols ∂f and ∂x_1 should not be confused with the ordinary differentials dy and dx, which may be treated as algebraic quantities and whose ratio dy/dx is the ordinary derivative. In $(\partial f/\partial x_1)_{x_2 \ldots x_n}$, ∂f indicates that some function f of several variables is to be partially differentiated with respect to the one of these variables which is indicated in ∂x_1, the remaining variables in the function, as indicated in the subscript, being held constant. Clearly, ∂f standing alone has no definite meaning, for f may be partially differentiated with respect to any one of its arguments x_1, x_2 . . . x_n. Until it is indicated by ∂x_1 which of the n partial derivatives is to be taken, ∂f has only an indefinite operational significance.

As a symbol for a partial derivative, $(\partial f/\partial x_1)_{x_2 \ldots x_n}$ must indicate clearly three things if its meaning is to be definite. These are:

1. The function that is to be differentiated f.
2. The variable x_1 with respect to which differentiation is to be performed.
3. The variables that are to be held constant during the differentiation (usually indicated as subscripts).

Unfortunately, ambiguity is often present in 1 and 3. In the case of 3, the subscripts are often omitted in cases where there may be some doubt as to which variables are really being held constant. In the case of 1, the functional symbol f is often replaced by the dependent variable w to give $\partial w/\partial x_1$, even though this dual notation may lead to great confusion when w is a

function not only of $x_1, x_2 \ldots x_n$ but also of some other group of variables. To illustrate the type of confusion that often occurs, let us consider a case from thermodynamics where

$$p = f_1(V,T) \tag{2}$$

and

$$V = f_2(S,T) \tag{3}$$

By substituting for V in (2) from (3), p becomes a function of S and T alone which may be written

$$p = f_1[f_2(S,T),T] = f_3(S,T) \tag{4}$$

It is now required to find the partial derivative of p with respect to T at constant S. By the methods of Par. 75

$$\left(\frac{\partial p}{\partial T}\right)_S = \left(\frac{\partial f_1}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_S + \left(\frac{\partial f_1}{\partial T}\right)_V \tag{5}$$

If f_1 is replaced by the dependent variable p and the subscripts are omitted, there results

$$\left(\frac{\partial p}{\partial T}\right) = \left(\frac{\partial p}{\partial V}\right)\left(\frac{\partial V}{\partial T}\right) + \left(\frac{\partial p}{\partial T}\right) \tag{6}$$

In (6), the two terms $\partial p \ \partial T$ would seem to eliminate each other and if in addition the temptation exists to treat ∂V as a quantity which may be canceled, the result is $\partial p, \partial T = 0$. There is small likelihood of the less ambiguous notation in (5) ever leading to such a result.

On the other hand, in dealing with Eq. (2) alone, when no auxiliary equations such as (3) are concerned, no confusion can result from writing either $\partial p \ \partial T$ or $\partial f_1 \ \partial T$ interchangeably and with omission of subscripts, the only other independent variable concerned in addition to T is V, and therefore V must be held constant during the differentiation indicated by $\partial f_1/\partial T$.

72. Partial Derivatives of Higher Order. Independence of the Order of Differentiation. The two first partial derivatives of the function

$$w = (x^2 + y^2)^n \tag{7}$$

are

$$\frac{\partial w}{\partial x} = n(x^2 + y^2)^{n-1}(2x) \tag{8}$$

and

$$\frac{\partial w}{\partial y} = n(x^2 + y^2)^{n-1}(2y) \tag{9}$$

Each first partial derivative being a function of x and y may be differentiated partially with respect to x and y to yield second-order partial derivatives. The second partial derivatives of (8) with respect to x are

$$\frac{\partial}{\partial x}\left(\frac{\partial w}{\partial x}\right) = \frac{\partial^2 w}{\partial x^2} = n(x^2 + y^2)^{n-1}(2) + n(n-1)(x^2 + y^2)^{n-2}(4x^2) \tag{10}$$

$$\frac{\partial}{\partial x}\left(\frac{\partial w}{\partial y}\right) = \frac{\partial^2 w}{\partial x \cdot \partial y} = 2yn(n-1)(x^2 + y^2)^{n-2}(2x) \tag{11}$$

The second partial derivatives of (9) with respect to y are

$$\frac{\partial}{\partial y}\left(\frac{\partial w}{\partial x}\right) = \frac{\partial^2 w}{\partial y \cdot \partial x} = 2xn(n-1)(x^2 + y^2)^{n-2}(2y) \tag{12}$$

$$\frac{\partial}{\partial y}\left(\frac{\partial w}{\partial y}\right) = \frac{\partial^2 w}{\partial y^2} = n(x^2 + y^2)^{n-1}(2) + n(n-1)(x^2 + y^2)^{n-2}(4y^2) \tag{13}$$

Comparison of (11) and (12) indicates that

$$\frac{\partial^2 w}{\partial y\, \partial x} = \frac{\partial^2 w}{\partial x\, \partial y} \tag{14}$$

It can be demonstrated with rigor that for any number of differentiations or variables the order of differentiation in the higher partial derivatives is immaterial.

73. The Relation between Partial Derivatives and Partial Differentials. It will be recalled from Par. 8 that a function u of two variables, $u = f(x,y)$ has a partial differential with respect to each variable. These are written

$$d_x f^* = d_x u^* = \left(\frac{\partial u}{\partial x}\right)_y \cdot dx \tag{15}$$

$$d_y f = d_y u = \left(\frac{\partial u}{\partial y}\right)_x \cdot dy \tag{16}$$

* In this notation for partial differentials the subscript denotes the variable with respect to which differentiation is performed and *not* the variable held constant.

Similar definitions hold for the n partial differentials of a function of n variables.

Upon dividing both sides of (15) by dx, there is obtained

$$\frac{d_x f}{dx} = \frac{d_x u}{dx} = \frac{(\partial u/\partial x)_y dx}{dx} = \left(\frac{\partial u}{\partial x}\right)_y \tag{17}$$

It therefore becomes proper to regard the partial derivative as the ratio of a partial differential $d_x u$ to the differential dx of the independent variable with respect to which the partial differentiation is performed.

Similarly, the partial differential of u with respect to y is

$$d_y f = d_y u = \left(\frac{\partial u}{\partial y}\right)_x dy$$

and

$$\frac{d_y f}{dy} = \frac{d_y u}{dy} = \frac{(\partial u/\partial y)_x dy}{dy} = \left(\frac{\partial u}{\partial y}\right)_x \tag{18}$$

Let us now solve the function $u = f(x,y)$ for y, obtaining $y = \phi(u,x)$. The partial differential of y with respect to x is

$$\frac{d_x \phi}{dx} = \frac{d_x y}{dx} = \frac{(\partial y/\partial x)_u dx}{dx} = \left(\frac{\partial y}{\partial x}\right)_u \tag{19}$$

Combining (18) and (19) by multiplication and employing the several notations, we have

$$\left(\frac{d_y f}{dy}\right)\left(\frac{d_x \phi}{dx}\right) = \left(\frac{d_y u}{dy}\right) \cdot \left(\frac{d_x y}{dx}\right) = \left(\frac{\partial u}{\partial y}\right)_x \cdot \left(\frac{\partial y}{\partial x}\right)_u \tag{20}$$

These equations emphasize the point that the terms ∂y in $(\partial u/\partial y)_x(\partial y/\partial x)_u$ cannot be canceled to give $(\partial u/\partial x)_y$* and that ∂y in $(\partial u\ \partial y)_x$ has an entirely different significance from ∂y in $(\partial y\ \partial x)_u$. In the case of $(\partial u\ \partial y)_x$, ∂y represents the differential of y considered as an independent variable in the equation $u = f(x,y)$, whereas ∂y in $(\partial y/\partial x)_u$ stands for the partial differential with respect to x of the function $y = \phi(u,x)$. It is possible to avoid confusion of this sort by utilizing the functional symbols f and ϕ and writing $(\partial f\ \partial y)_x$ instead of $(\partial u\ \partial y)_x$ and $(\partial \phi\ \partial x)_u$ instead of $(\partial y\ \partial x)_u$. It should be realized, however, that the latter notation in both cases is widely used in spite of its ambiguity.

* It is shown in Par. 77 that $(\partial u/\partial y)_x(\partial y/\partial x)_u = -(\partial u/\partial x)_y$.

74. Differentiation of Composite Functions. The differential of a function of any number of variables

$$w = f(x_1, x_2 \cdot \cdot \cdot x_n) \tag{21}$$

is given by

$$dw = df = \frac{\partial f}{\partial x_1} dx_1 + \frac{\partial f}{\partial x_2} dx_2 + \cdot \cdot \cdot \frac{\partial f}{\partial x_n} \cdot dx_n \tag{22}$$

If x_1, x_2 . . . x_n are each functions of a single independent variable t as given by the equations

$$x_1 = f_1(t),\ x_2 = f_2(t),\ \cdot \cdot \cdot\ x_n = f_n(t)$$

the differentials dx_1, dx_2 . . . dx_n are given by

$$\left.\begin{aligned} dx_1 &= f_1'(t)dt = \frac{df_1(t)}{dt}dt = \frac{dx_1}{dt}dt \\ dx_2 &= f_2'(t)dt = \frac{df_2(t)}{dt}dt = \frac{dx_2}{dt}dt \\ dx_n &= f_n'(t)dt = \frac{df_n(t)}{dt}dt = \frac{dx_n}{dt}dt \end{aligned}\right\} \tag{23}$$

the three notations being used interchangeably.

Substituting in (22) results in

$$dw = \left[\left(\frac{\partial f}{\partial x_1}\right)\frac{dx_1}{dt} + \left(\frac{\partial f}{\partial x_2}\right)\frac{dx_2}{dt} + \cdot \cdot \cdot \left(\frac{\partial f}{\partial x_n}\right)\frac{dx_n}{dt}\right]dt \tag{24}$$

Division by dt gives

$$\frac{dw}{dt} = \frac{\partial f}{\partial x_1}\frac{dx_1}{dt} + \frac{\partial f}{\partial x_2}\frac{dx_2}{dt} + \cdot \cdot \cdot \frac{\partial f}{\partial x_n} \cdot \frac{dx_n}{dt} \tag{25}$$

Since the arguments x_1, x_2 . . . x_n of the original function are each functions of t, w is in reality a function of a single variable t, and the derivative of w with respect to t is an ordinary derivative. When the arguments of a function w are themselves functions of other variables, w is said to be a composite function.

Let us assume that in $w = f(x_1, x_2 \cdot \cdot \cdot x_n)$, x_1, $x_2 \cdot \cdot \cdot x_n$ are each functions of two variables t and s, the functional relationships being given by the equations

$$\left.\begin{aligned} x_1 &= \phi_1(t,s) \\ x_2 &= \phi_2(t,s) \\ x_n &= \phi_n(t,s) \end{aligned}\right\} \tag{26}$$

The differentials of $x_1, x_2 \ldots x_n$ are

$$\left.\begin{aligned} dx_1 &= \frac{\partial x_1}{\partial t}dt + \frac{\partial x_1}{\partial s}ds \\ dx_2 &= \frac{\partial x_2}{\partial t}dt + \frac{\partial x_2}{\partial s}ds \\ dx_n &= \frac{\partial x_n}{\partial t}dt + \frac{\partial x_n}{\partial s}ds \end{aligned}\right\} \tag{27}$$

Substituting in (22) gives

$$dw = df = \left(\frac{\partial f}{\partial x_1}\frac{\partial x_1}{\partial t} + \frac{\partial f}{\partial x_2}\cdot\frac{\partial x_2}{\partial t} + \cdots \frac{\partial f}{\partial x_n}\frac{\partial x_n}{\partial t}\right)dt + \left(\frac{\partial f}{\partial x_1}\cdot\frac{\partial x_1}{\partial s} + \frac{\partial f}{\partial x_2}\cdot\frac{\partial x_2}{\partial s} + \cdots \frac{\partial f}{\partial x_n}\frac{\partial x_n}{\partial s}\right)ds \tag{28}$$

But w is also a function of t and s which may be obtained by eliminating $x_1, x_2 \ldots x_n$ in (21) by Eqs. (26). This may be written

$$w = f[\phi_1(t,s),\phi_2(t,s) \cdots \phi_n(t,s)] = F(t,s) \tag{29}$$

and

$$dw = dF = df = \frac{\partial w}{\partial t}dt + \frac{\partial w}{\partial s}ds = \frac{\partial f}{\partial t}dt + \frac{\partial f}{\partial s}ds = \frac{\partial F}{\partial t}dt + \frac{\partial F}{\partial s}ds \tag{30}$$

Comparing (28) and (30), we obtain the partial derivatives of w with respect to t and s by equating the coefficients of dt and ds. In the case of t,

$$\frac{\partial w}{\partial t} = \frac{\partial f}{\partial x_1}\frac{\partial x_1}{\partial t} + \frac{\partial f}{\partial x_2}\frac{\partial x_2}{\partial t} + \cdots \frac{\partial f}{\partial x_n}\frac{\partial x_n}{\partial t} \tag{31}$$

Attention is again drawn to the question of notation in Eq. (28). There is really no need to place subscripts on the quantities $\partial f/\partial x_1$, $\partial f/\partial x_2$, $\partial f/\partial x_n$, because during the operation of differentiating the function f with respect to one of its arguments $x_1, x_2 \ldots x_n$ the rest of these must be held constant. Similarly, there is no real need to employ subscripts on $\partial x_1/\partial t \ldots \partial x_n/\partial t$ and $\partial x_1/\partial s \ldots \partial x_n/\partial s$, again for the reason that differentiation of x_1 with respect to one of its arguments t or s necessitates constancy of the other. On the other hand, the function $f(x_1,x_2 \ldots x_n)$ being a function of t and s as given by (29) may

be differentiated with respect to t at constant s, with $x_1, x_2 \ldots x_n$ permitted to vary in accordance with Eqs. (27). In this case, the nature of the differentiation would be better indicated by $\partial F/\partial t$ than by $\partial f/\partial t$ since t is an argument of F and not of f [see (29)]. It would be correct for $\partial w/\partial x_1$ to replace $\partial f/\partial x_1$ and $\partial w/\partial t$ to replace $\partial F/\partial t$ since w refers to both functions.

Equation (31) could have been obtained directly from (28) by holding s constant and dividing each side by dt. Under this circumstance, ds becomes equal to zero, and the last term on the right vanishes. It is important to note that no meaning is assigned to the symbol dw/dt, which would result from mere division of (28) by dt. If there are n independent variables, a derivative may be defined only by keeping $n - 1$ of these constant. Therefore, because there are two independent variables in (28) t and s, division by dt must be at constant s to give $\partial w/\partial t$. Division by differentials must be thoroughly understood, as it is of great utility in the applications of partial differentiation in thermodynamics.

75. Summary of Important Cases of Differentiation of Composite Functions. Equations (22), (25), and (31) are the fundamental formulas of partial differentiation. They will now be applied to several composite functions of frequent occurrence.

CASE I. $w = f(x)$ and $x = F(u)$. Application of (25) yields the first derivative

$$\frac{dw}{du} = \frac{df}{dx}\frac{dx}{du} \tag{32}$$

The second derivative is

$$\frac{d}{du}\left(\frac{dw}{du}\right) = \frac{d^2w}{du^2} = \frac{df}{dx}\frac{d^2x}{du^2} + \frac{dx}{du}\frac{d}{du}\left(\frac{df}{dx}\right) \tag{33}$$

The first derivative df/dx is itself a function of x, usually written $f'(x)$. The term $d(df/dx)/du$ is then evaluated by application of (25) as

$$\frac{d^2f}{dx^2}\frac{dx}{du}$$

whence

$$\frac{d^2w}{du^2} = \frac{df}{dx}\cdot\frac{d^2x}{du^2} + \left(\frac{dx}{du}\right)^2\frac{d^2f}{dx^2} \tag{34}$$

Example: $w = x^n$ and $x = u^2 - 2$

$$\frac{df}{dx} = nx^{n-1}; \qquad \frac{dx}{du} = 2u$$

$$\frac{dw}{du} = (nx^{n-1})(2u) = n(u^2 - 2)^{n-1}(2u)$$

$$\frac{d^2f}{dx^2} = n(n-1)x^{n-2}; \qquad \frac{d^2x}{du^2} = 2$$

$$\frac{d^2w}{du^2} = nx^{n-1}(2) + (2u)^2 n(n-1)x^{n-2}$$

CASE II. $w = f(x)$ and $x = F(u,v)$. Application of (31) yields the two first partial derivatives

$$\frac{\partial w}{\partial u} = \frac{df}{dx}\frac{\partial x}{\partial u}; \qquad \frac{\partial w}{\partial v} = \frac{df}{dx}\frac{\partial x}{\partial v} \tag{35}$$

$$\frac{\partial^2 w}{\partial u^2} = \frac{df}{dx}\frac{\partial}{\partial u}\left(\frac{\partial x}{\partial u}\right) + \frac{\partial x}{\partial u}\frac{\partial}{\partial u}\left(\frac{df}{dx}\right) \tag{36}$$

$\partial(df/dx)/\partial u$ is evaluated by noting that df/dx is itself a function of x so that (31) may be applied to give

$$\frac{\partial}{\partial u}\left(\frac{df}{dx}\right) = \frac{d(df/dx)}{dx}\frac{\partial x}{\partial u} = \frac{d^2f}{dx^2}\frac{\partial x}{\partial u}$$

By substitution, (36) now becomes

$$\frac{\partial^2 w}{\partial u^2} = \frac{df}{dx}\frac{\partial^2 x}{\partial u^2} + \left(\frac{\partial x}{\partial u}\right)^2\frac{d^2f}{dx^2} \tag{37}$$

The other two second-order derivatives are obtained in similar fashion and are

$$\frac{\partial^2 w}{\partial u\,\partial v} = \frac{df}{dx}\frac{\partial^2 x}{\partial u\,\partial v} + \frac{\partial x}{\partial u}\frac{\partial x}{\partial v}\frac{d^2f}{dx^2} \tag{38}$$

$$\frac{\partial^2 w}{\partial v^2} = \frac{df}{dx}\frac{\partial^2 x}{\partial v^2} + \left(\frac{\partial x}{\partial v}\right)^2\frac{d^2f}{dx^2} \tag{39}$$

Example: $w = (x+3)^2$ and $x = u^2 - v^2$

$$\frac{df}{dx} = 2(x+3); \qquad \frac{\partial x}{\partial u} = 2u; \qquad \frac{\partial x}{\partial v} = -2v;$$

$$\frac{d^2f}{dx^2} = 2; \qquad \frac{\partial^2 x}{\partial u^2} = 2; \qquad \frac{\partial^2 x}{\partial v^2} = -2;$$

$$\frac{\partial^2 x}{\partial u \cdot \partial v} = \frac{\partial}{\partial v}\left(\frac{\partial x}{\partial u}\right) = \frac{\partial}{\partial u}\left(\frac{\partial x}{\partial v}\right) = 0$$

Substitution in (37), (38), and (39) gives

$$\frac{\partial^2 w}{\partial u^2} = 2(x+3)(2) + 2(2u)^2$$

$$\frac{\partial^2 w}{\partial u\,\partial v} = 2(x+3)(0) + (2u)(-2v)(2) = -8uv$$

$$\frac{\partial^2 w}{\partial v^2} = 2(x+3)(-2) + 2(-2v)^2$$

CASE III. $w = f(x,y)$; $x = F_1(u)$, $y = F_2(u)$. There is but one first derivative in this case, since w is a function of u only. By application of (25)

$$\frac{dw}{du} = \frac{\partial f}{\partial x}\frac{dx}{du} + \frac{\partial f}{\partial y}\frac{dy}{du} \tag{40}$$

Application of (25) to each term of (40) yields the second partial derivative

$$\frac{d^2 w}{du^2} = \frac{\partial f}{\partial x}\frac{d^2 x}{du^2} + \frac{dx}{du}\frac{d}{du}\left(\frac{\partial f}{\partial x}\right) + \frac{\partial f}{\partial y}\frac{d^2 y}{du^2} + \frac{dy}{du}\frac{d}{du}\left(\frac{\partial f}{\partial y}\right) \tag{41}$$

But $\partial f/\partial x$ and $\partial f/\partial y$ are each functions of x and y, and (25) may be applied to each of them as follows:

$$\frac{d}{du}\left(\frac{\partial f}{\partial x}\right) = \frac{\partial(\partial f/\partial x)}{\partial x}\frac{dx}{du} + \frac{\partial(\partial f/\partial x)}{\partial y}\frac{dy}{du} = \frac{\partial^2 f}{\partial x^2}\frac{dx}{du} + \frac{\partial^2 f}{\partial y\,\partial x}\frac{dy}{du} \tag{42}$$

$$\frac{d}{du}\left(\frac{\partial f}{\partial y}\right) = \frac{\partial(\partial f/\partial y)}{\partial x}\frac{dx}{du} + \frac{\partial(\partial f/\partial y)}{\partial y}\frac{dy}{du} = \frac{\partial^2 f}{\partial x\,\partial y}\frac{dx}{du} + \frac{\partial^2 f}{\partial y^2}\frac{dy}{du} \tag{43}$$

Substituting in (41) gives

$$\frac{d^2 w}{du^2} = \frac{\partial f}{\partial x}\frac{d^2 x}{du^2} + \frac{\partial^2 f}{\partial x^2}\left(\frac{dx}{du}\right)^2 + 2\frac{\partial^2 f}{\partial x\,\partial y}\frac{dx}{du}\frac{dy}{du} + \frac{\partial f}{\partial y}\frac{d^2 y}{du^2} + \frac{\partial^2 f}{\partial y^2}\left(\frac{dy}{du}\right)^2 \tag{44}$$

Example: $w = x^2 + y^2$; $x = u^3$; $y = u^2$.

$$\frac{\partial f}{\partial x} = \frac{\partial(x^2+y^2)}{\partial x} = 2x; \qquad \frac{\partial f}{\partial y} = 2y; \qquad \frac{dx}{du} = 3u^2; \qquad \frac{dy}{du} = 2u.$$

$$\frac{dw}{du} = 2x(3u^2) + 2y(2u)$$

$$\frac{\partial^2 f}{\partial x^2} = 2; \qquad \frac{\partial^2 f}{\partial y^2} = 2; \qquad \frac{\partial f}{\partial x\,\partial y} = 0; \qquad \frac{d^2 x}{du^2} = 6u; \qquad \frac{d^2 y}{du^2} = 2$$

$$\frac{d^2 w}{du^2} = 2x(6u) + 2(3u^2)^2 + 2(0)(3u^2)(2u) + 2y(2) + 2(2u)^2$$

CASE IV. $w = f(x,y)$ where $x = f_1(u)$, $y = f_2(v)$. By application of (31),

$$\frac{\partial w}{\partial u} = \frac{\partial f}{\partial x}\frac{\partial x}{\partial u} + \frac{\partial f}{\partial y}\frac{\partial y}{\partial u} \tag{45}$$

In this case, $y = f_2(v)$ is independent of u, and hence $\partial y / \partial u$ vanishes. Due to the fact that x is a function of a single variable u, $\partial x / \partial u$ becomes the ordinary derivative dx / du. Equation (45) then becomes

$$\frac{\partial w}{\partial u} = \frac{\partial f}{\partial x}\frac{dx}{du} \tag{46}$$

Similarly, when x is held constant,

$$\frac{\partial w}{\partial v} = \frac{\partial f}{\partial y}\frac{dy}{dv} \tag{47}$$

$$\frac{\partial^2 w}{\partial u^2} = \frac{\partial f}{\partial x}\frac{d^2x}{du^2} + \frac{dx}{du}\frac{\partial}{\partial u}\left(\frac{\partial f}{\partial x}\right)$$

But $\partial f / \partial x$ is a function of x and y, so that (25) may be applied to give

$$\frac{\partial}{\partial u}\left(\frac{\partial f}{\partial x}\right) = \frac{\partial^2 f}{\partial x^2}\cdot\frac{dx}{du}$$

and

$$\frac{\partial^2 w}{\partial u^2} = \frac{\partial f}{\partial x}\frac{d^2x}{du^2} + \frac{\partial^2 f}{\partial x^2}\left(\frac{dx}{du}\right)^2 \tag{48}$$

Similarly,

$$\frac{\partial^2 w}{\partial v^2} = \frac{\partial f}{\partial y}\frac{d^2y}{dv^2} + \frac{\partial^2 f}{\partial y^2}\left(\frac{dy}{dv}\right)^2 \tag{49}$$

and

$$\frac{\partial^2 w}{\partial u\,\partial v} = \frac{dx}{du}\frac{dy}{dv}\frac{\partial^2 f}{\partial x\,\partial y} \tag{50}$$

This case is frequently of importance in effecting simplification in a formula by change of the independent variables.

Example : Simplify the equation $ax(\partial\phi/\partial x)_y + by(\partial\phi/\partial y)_x = 0$, where a and b are constants and ϕ is a function of x and y.

Place $x = u^a$, $y = v^b$.

$$\left(\frac{\partial\phi}{\partial u}\right)_v = \left(\frac{\partial\phi}{\partial x}\right)_y\frac{dx}{du} = \left(\frac{\partial\phi}{\partial x}\right)_y au^{a-1} = \left(\frac{\partial\phi}{\partial x}\right)_y\frac{ax}{u}$$

and

$$ax\left(\frac{\partial \phi}{\partial x}\right)_y = u\left(\frac{\partial \phi}{\partial u}\right)_v$$

Similarly,

$$by\left(\frac{\partial \phi}{\partial y}\right)_x = v\left(\frac{\partial \phi}{\partial v}\right)_u$$

The simplified equation is

$$u\left(\frac{\partial \phi}{\partial u}\right)_v + v\left(\frac{\partial \phi}{\partial v}\right)_u = 0$$

CASE V. $w = f(x,y)$; $x = F_1(u,v)$, $y = F_2(u,v)$. Application of (31) gives the two first partial derivatives

$$\frac{\partial w}{\partial u} = \frac{\partial f}{\partial x}\frac{\partial x}{\partial u} + \frac{\partial f}{\partial y}\frac{\partial y}{\partial u} \tag{51}$$

$$\frac{\partial w}{\partial v} = \frac{\partial f}{\partial x}\frac{\partial x}{\partial v} + \frac{\partial f}{\partial y}\frac{\partial y}{\partial v} \tag{52}$$

The second partial derivatives are obtained by differentiating (51) and (52).

$$\frac{\partial^2 w}{\partial u^2} = \frac{\partial f}{\partial x}\frac{\partial^2 x}{\partial u^2} + \frac{\partial x}{\partial u}\frac{\partial}{\partial u}\left(\frac{\partial f}{\partial x}\right) + \frac{\partial f}{\partial y}\frac{\partial^2 y}{\partial u^2} + \frac{\partial y}{\partial u}\frac{\partial}{\partial u}\left(\frac{\partial f}{\partial y}\right)$$

But $\partial f/\partial x$ and $\partial f/\partial y$ being functions of x and y may be treated by (31) to give

$$\frac{\partial}{\partial u}\left(\frac{\partial f}{\partial x}\right) = \frac{\partial^2 f}{\partial x^2}\frac{\partial x}{\partial u} + \frac{\partial^2 f}{\partial x\,\partial y}\frac{\partial y}{\partial u} \tag{53}$$

$$\frac{\partial}{\partial u}\left(\frac{\partial f}{\partial y}\right) = \frac{\partial^2 f}{\partial y\,\partial x}\frac{\partial x}{\partial u} + \frac{\partial^2 f}{\partial y^2}\frac{\partial y}{\partial u} \tag{54}$$

Substituting in (53) yields

$$\frac{\partial^2 w}{\partial u^2} = \frac{\partial f}{\partial x}\frac{\partial^2 x}{\partial u^2} + \frac{\partial^2 f}{\partial x^2}\left(\frac{\partial x}{\partial u}\right)^2 + 2\frac{\partial^2 f}{\partial x\,\partial y}\cdot\frac{\partial x}{\partial u}\cdot\frac{\partial y}{\partial u} + \frac{\partial f}{\partial y}\frac{\partial^2 y}{\partial u^2} + \frac{\partial^2 f}{\partial y^2}\left(\frac{\partial y}{\partial u}\right)^2 \tag{55}$$

Obviously the formula for $\partial^2 w/\partial v^2$ is the same as (55) with v substituted for u. The third partial derivative of the second order is obtained by applying (31) to either (51) or (52).

$$\frac{\partial^2 w}{\partial u\,\partial v} = \frac{\partial f}{\partial x}\frac{\partial^2 x}{\partial u\,\partial v} + \frac{\partial x}{\partial v}\frac{\partial}{\partial u}\left(\frac{\partial f}{\partial x}\right) + \frac{\partial f}{\partial y}\frac{\partial^2 y}{\partial u\partial v} + \frac{\partial y}{\partial v}\frac{\partial}{\partial u}\left(\frac{\partial f}{\partial y}\right)$$

Substituting from (53) and (54) results in

$$\frac{\partial^2 w}{\partial u\,\partial v} = \frac{\partial f}{\partial x}\frac{\partial^2 x}{\partial u\,\partial v} + \frac{\partial^2 f}{\partial x^2}\frac{\partial x}{\partial u}\frac{\partial x}{\partial v} + \frac{\partial^2 f}{\partial x\,\partial y}\frac{\partial y}{\partial u}\frac{\partial x}{\partial v} + \frac{\partial f}{\partial y}\frac{\partial^2 y}{\partial u\,\partial v} + \frac{\partial y}{\partial v}\frac{\partial x}{\partial u}\frac{\partial^2 f}{\partial x\,\partial y} + \frac{\partial^2 f}{\partial y^2}\frac{\partial y}{\partial v}\frac{\partial y}{\partial u} = \frac{\partial^2 x}{\partial u\,\partial v}\frac{\partial f}{\partial x} + \frac{\partial^2 y}{\partial u\,\partial v}\frac{\partial f}{\partial y} + \frac{\partial^2 f}{\partial x\,\partial y}\left[\frac{\partial y}{\partial v}\frac{\partial x}{\partial u} + \frac{\partial y}{\partial u}\frac{\partial x}{\partial v}\right] + \frac{\partial^2 f}{\partial x^2}\frac{\partial x}{\partial u}\frac{\partial x}{\partial v} + \frac{\partial^2 f}{\partial y^2}\frac{\partial y}{\partial u}\frac{\partial y}{\partial v} \tag{56}$$

An important application of Case V occurs in the change of coordinate systems.

76. Change from Cartesian to Cylindrical Coordinates. The relation between these two systems may be seen in Fig. 42. To specify a point in cylindrical coordinates, drop a perpendicular to OX. The cylindrical coordinates of P are: x, r = length of perpendicular from P to OX, and ϕ, the angle made by the perpendicular and plane XOY. The following geometrical relations between the two systems of coordinates must hold:

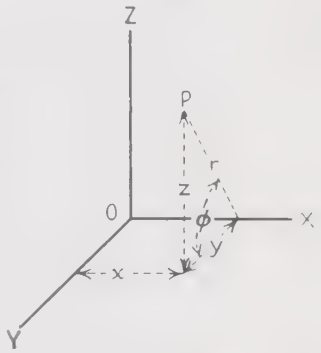

FIG. 42.—Cylindrical coordinates.

$$x = x \tag{57}$$

$$y = r\cos\phi \tag{58}$$

$$z = r\sin\phi \tag{59}$$

$$r = \sqrt{y^2 + z^2} \tag{60}$$

Cylindrical coordinates are particularly well adapted to treating the problem of heat transmission in a circular cylinder, the axis of which is coincident with OX. The treatment of this case, described in Chap. VI, starts from the general unsteady-state heat-transfer equation in Cartesian coordinates,

$$\frac{\partial t}{\partial \theta} = \alpha\left(\frac{\partial^2 t}{\partial x^2} + \frac{\partial^2 t}{\partial y^2} + \frac{\partial^2 t}{\partial z^2}\right)$$

and proceeds to cylindrical coordinates for solution because of the resulting simplification of boundary conditions.

For a given value of θ and x, t is some function of y and z, which may be written $f(y,z)$. Since $y = F_1(r,\phi) = r\cos\phi$ and $z = F_2(r,\phi) = r\sin\phi$, t is some function of r and ϕ, which may be written $t = \psi(r,\phi)$. Furthermore, r and ϕ are each functions of y and z and may be written $r = F_3(y,z)$ and $\phi = F_4(y,z)$. The application of Case V is now apparent, and the required

transformation is easily effected by substitution into (51) and (55) with the changes in notation $w = t = \psi(r,\phi)$, $x = r$, $y = \phi$, $u = y$, $v = z$. The following partial derivatives are used throughout the calculation; so they will be computed immediately for convenient reference.

$$\frac{\partial r}{\partial y} = \frac{1}{2\sqrt{y^2 + z^2}}(2y) = \frac{r\cos\phi}{r} = \cos\phi \tag{61}$$

$$\frac{\partial r}{\partial z} = \frac{1}{2\sqrt{y^2 + z^2}}(2z) = \frac{r\sin\phi}{r} = \sin\phi \tag{62}$$

The quotient of (62) and (61) is

$$\tan\phi = \frac{z}{y} \qquad \text{from which} \qquad \phi = \tan^{-1}\frac{z}{y} \tag{63}$$

$$\frac{\partial\phi}{\partial y} = \frac{1}{1 + (z/y)^2}(z)\left(-\frac{1}{y^2}\right) = -\frac{z}{y^2 + z^2} = -\frac{r\sin\phi}{r^2} = -\frac{\sin\phi}{r} \tag{64}$$

$$\frac{\partial\phi}{\partial z} = \frac{1}{y}\left(\frac{1}{1 + (z/y)^2}\right) = \frac{y}{y^2 + z^2} = \frac{r\cos\phi}{r^2} = \frac{\cos\phi}{r} \tag{65}$$

$$\frac{\partial^2 r}{\partial y^2} = -\sin\phi\frac{\partial\phi}{\partial y} = \frac{\sin^2\phi}{r} \tag{66}$$

$$\frac{\partial^2 r}{\partial z^2} = \cos\phi\frac{\partial\phi}{\partial z} = \frac{\cos^2\phi}{r} \tag{67}$$

$$\frac{\partial^2\phi}{\partial y^2} = -\frac{\partial}{\partial y}\left(\frac{z}{y^2 + z^2}\right) = \frac{2yz}{(y^2 + z^2)^2} \tag{68}$$

$$\frac{\partial^2\phi}{\partial z^2} = \frac{\partial}{\partial z}\left(\frac{y}{y^2 + z^2}\right) = \frac{-2yz}{(y^2 + z^2)^2} \tag{69}$$

$$\frac{\partial^2 t}{\partial y^2} = \frac{\partial t}{\partial r}\frac{\partial^2 r}{\partial y^2} + \frac{\partial^2 t}{\partial r^2}\left(\frac{\partial r}{\partial y}\right)^2 + 2\frac{\partial^2 t}{\partial r\,\partial\phi}\frac{\partial r}{\partial y}\frac{\partial\phi}{\partial y} + \frac{\partial t}{\partial\phi}\frac{\partial^2\phi}{\partial y^2} + \frac{\partial^2 t}{\partial\phi^2}\left(\frac{\partial\phi}{\partial y}\right)^2 \tag{70}$$

$$\frac{\partial^2 t}{\partial z^2} = \frac{\partial t}{\partial r}\frac{\partial^2 r}{\partial z^2} + \frac{\partial^2 t}{\partial r^2}\left(\frac{\partial r}{\partial z}\right)^2 + 2\frac{\partial^2 t}{\partial r\,\partial\phi}\frac{\partial r}{\partial z}\frac{\partial\phi}{\partial z} + \frac{\partial t}{\partial\phi}\frac{\partial^2\phi}{\partial z^2} + \frac{\partial^2 t}{\partial\phi^2}\left(\frac{\partial\phi}{\partial z}\right)^2 \tag{71}$$

When these two equations are combined,

$$\begin{aligned}\frac{\partial^2 t}{\partial y^2} + \frac{\partial^2 t}{\partial z^2} = {} & \frac{\partial t}{\partial r}\left[\frac{\partial^2 r}{\partial y^2} + \frac{\partial^2 r}{\partial z^2}\right] + \frac{\partial^2 t}{\partial r^2}\left[\left(\frac{\partial r}{\partial y}\right)^2 + \left(\frac{\partial r}{\partial z}\right)^2\right] + \\ & 2\frac{\partial^2 t}{\partial r\,\partial\phi}\left[\frac{\partial r}{\partial y}\frac{\partial\phi}{\partial y} + \frac{\partial r}{\partial z}\frac{\partial\phi}{\partial z}\right] + \frac{\partial t}{\partial\phi}\left[\frac{\partial^2\phi}{\partial y^2} + \frac{\partial^2\phi}{\partial z^2}\right] \\ & + \frac{\partial^2 t}{\partial\phi^2}\left[\left(\frac{\partial\phi}{\partial y}\right)^2 + \left(\frac{\partial\phi}{\partial z}\right)^2\right]\end{aligned} \tag{72}$$

All the derivatives in brackets have already been computed. Substituting their values from Eqs. (61) to (69) gives

$$\frac{\partial^2 t}{\partial y^2} + \frac{\partial^2 t}{\partial z^2} = \frac{\partial t}{\partial r}\left[\frac{\sin^2 \phi + \cos^2 \phi}{r}\right] + \frac{\partial^2 t}{\partial r^2}[\cos^2 \phi + \sin^2 \phi] + 2\frac{\partial^2 t}{\partial r\, \partial \phi}\left[\cos \phi\left(-\frac{\sin \phi}{r}\right) + \sin \phi\left(\frac{\cos \phi}{r}\right)\right] + \frac{\partial t}{\partial \phi}\left[\frac{2yz}{(y^2 + z^2)^2} - \frac{2yz}{(y^2 + z^2)^2}\right] + \frac{\partial^2 t}{\partial \phi^2}\left[\frac{\sin^2 \phi + \cos^2 \phi}{r^2}\right] \quad (73)$$

Since $\sin^2 \phi + \cos^2 \phi = 1$, (73) becomes

$$\frac{\partial^2 t}{\partial y^2} + \frac{\partial^2 t}{\partial z^2} = \frac{1}{r}\frac{\partial t}{\partial r} + \frac{\partial^2 t}{\partial r^2} + \frac{1}{r^2}\frac{\partial^2 t}{\partial \phi^2} \quad (74)$$

The complete heat-transfer equation in cylindrical coordinates may now be written

$$\frac{\partial t}{\partial \theta} = \alpha\left(\frac{\partial^2 t}{\partial x^2} + \frac{1}{r}\frac{\partial t}{\partial r} + \frac{1}{r^2}\frac{\partial^2 t}{\partial \phi^2} + \frac{\partial^2 t}{\partial r^2}\right) \quad (75)$$

In the case of an infinite cylinder with its axis coincident with the x axis, conditions at every cross section perpendicular to the x axis are the same, and the term involving x drops from the equation.

77. Differentiation of Implicit Functions. If

$$f(x_1,x_2 \cdot \cdot \cdot x_n) = c,$$

where c is a constant, $df = 0$. When $c = 0$, $f(x_1,x_2 \cdot \cdot \cdot x_n)$ is said to be an implicit function. It is obvious that all the variables in $f(x_1,x_2 \cdot \cdot \cdot x_n) = 0$ cannot be independent unless it is an identity.

The methods of the preceding paragraphs may be applied to implicit functions and are frequently very useful in the differentiation of an implicit function of two variables. The differential of $f(x,y) = 0$ is

$$df = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy = 0 \quad (76)$$

Equation (76) yields for dy/dx the important relation

$$\frac{dy}{dx} = -\frac{\partial f/\partial x}{\partial f/\partial y} \quad (77)$$

Several interesting relations are obtained from the differentiation of a function of three variables $f(x,y,z) = 0$. If (22) is applied

$$df = \left(\frac{\partial f}{\partial x}\right)_{y,z} dx + \left(\frac{\partial f}{\partial y}\right)_{x,z} dy + \left(\frac{\partial f}{\partial z}\right)_{x,y} dz = 0$$

By holding y constant, $dy = 0$, and

$$\left(\frac{\partial x}{\partial z}\right)_y = -\frac{(\partial f/\partial z)_{x,y}}{(\partial f/\partial x)_{y,z}} = \frac{1}{(\partial z/\partial x)_y} \tag{78}$$

with similar expressions for $(\partial z/\partial y)_x$ and $(\partial y/\partial x)_z$. These lead to the relations

$$\left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial z}{\partial y}\right)_x = -\left(\frac{\partial z}{\partial x}\right)_y \tag{79}$$

and

$$\left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial x}{\partial z}\right)_y = -1; \text{ etc.} \tag{80}$$

Analogous relationships may be obtained for a function of any number of variables. In particular, if we have the function $f(x_1,x_2,x_3 \cdots x_n) = 0$, it is possible to obtain the total differential

$$df = \frac{\partial f}{\partial x_1} dx_1 + \frac{\partial f}{\partial x_2} dx_2 + \frac{\partial f}{\partial x_3} dx_3 + \cdots \frac{\partial f}{\partial x_n} dx_n = 0 \tag{81}$$

By holding $x_3 \ldots x_n$ constant, there is obtained

$$\left(\frac{\partial x_1}{\partial x_2}\right)_{x_3 \ldots x_n} = -\frac{(\partial f/\partial x_2)_{x_1,x_3 \ldots x_n}}{(\partial f/\partial x_1)_{x_2,x_3 \ldots x_n}} \tag{82}$$

78. Applications to Equations of State of One-component Systems. It is an experimental fact that any two of the three variables temperature, pressure, and volume suffice to determine the physical state of a homogeneous fluid. Consequently, there must exist a functional relationship among these three properties of the general form

$$f(p,v,t) = 0 \tag{83}$$

Equation (83) is known as the equation of state of the fluid and may range in complexity from the simple gas law to a relation so complex as to be represented most satisfactorily

in the form of experimental curves. The relations of Par. 77 are applicable to the equation of state, and (80) becomes

$$\left(\frac{\partial p}{\partial v}\right)_t\left(\frac{\partial v}{\partial t}\right)_p\left(\frac{\partial t}{\partial p}\right)_v = -1 \tag{84}$$

or, alternatively,

$$\left(\frac{\partial p}{\partial v}\right)_t\left(\frac{\partial v}{\partial t}\right)_p = -\frac{1}{(\partial t/\partial p)_v} = -\left(\frac{\partial p}{\partial t}\right)_v = \frac{(\partial v/\partial t)_p}{(\partial v/\partial p)_t} \tag{85}$$

As an example of the utility of these relationships, we shall consider their application to the practical question of the magnitude of the pressure developed by heating a liquid that occupies the entire space in a closed reaction vessel. The liquid to be considered will be water initially at 40°C., heated to 50°C. If expansion of the vessel is neglected, the process may be considered to take place at constant volume and (85) may be integrated to give

$$p_2 - p_1 = -\int_{t_1}^{t_2}\frac{(\partial v/\partial t)_p}{(\partial v/\partial p)_t}dt \tag{86}$$

The literature reports two coefficients that are useful in the solution of this type of problem. The coefficient of cubical expansion is the ratio of the fractional increase in volume to the increase in temperature and may be written

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial t}\right)_p \tag{87}$$

Similarly, the coefficient of compressibility β is defined by the equation

$$\beta = \frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_t \tag{88}$$

In terms of these coefficients, (86) may be written

$$p_2 - p_1 = -\int_{t_1}^{t_2}\frac{\alpha}{\beta}dt \tag{89}$$

Both α and β are functions of pressure as well as temperature, and, strictly speaking, (89) is an integral equation. The variation in α and β may be taken into consideration and Δp obtained with as high a degree of accuracy as possible from the available data

by dividing the integral up into a series of integrals each taken over such a small temperature range that the coefficients may be taken as constant at their average values over the respective ranges. If α and β are considered constant at 0.30×10^{-3} $(°C.)^{-1}$ and -38×10^{-6} $(atm.)^{-1}$ (89) may be integrated from 40 to 50°C. to give

$$\Delta p = \frac{0.30 \times 10^{-3}}{38 \times 10^{-6}}(10) = \frac{3{,}000}{38} = 79 \text{ atm.}$$

79. Differentiation of Definite Integrals. Definite integrals may appear in the form

$$F(b) - F(a) = \int_a^b f(x,c)dx \tag{90}$$

where $F(x)$ is the integral function of $f(x,c)$, and a and b are

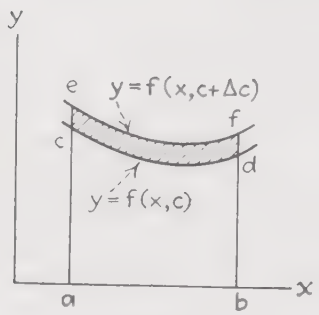

FIG. 43.

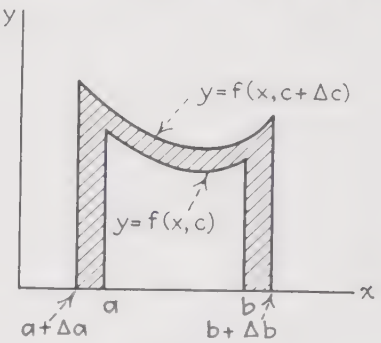

FIG. 44.

constant values of x; c is an arbitrary constant which remains constant during any one integration, but which may vary to form different integrals all taken between the same two limits. In such a case, the integral is a function of c and may be written

$$\phi(c) = \int_a^b f(x,c)dx \tag{91}$$

The function $\phi(c)$ is represented by the area *acdb* in Fig. 43. When c receives an increment Δc, $\phi(c + \Delta c)$ is the area *aefb* under the curve $y = f(x,c + \Delta c)$, and $\Delta\phi$ is represented by shaded area *ccfd*. It is often desirable to compute the rate of change of ϕ with respect to c, *i.e.*, $d\phi\ dc$. This is done by the formula

$$\frac{d\phi}{dc} = \int_a^b \frac{\partial f(x,c)}{\partial c}dx \tag{92}$$

When the limits of integration a and b are functions of c, an increment in c produces an increment in ϕ represented by the shaded area in Fig. 44. In this case, it may be shown that

$$\frac{d\phi}{dc} = \int_a^b \frac{\partial f(x,c)}{\partial c} dx + f(b,c)\frac{db}{dc} - f(a,c)\frac{da}{dc} \tag{93}$$

This type of differentiation has many possible uses in determining maxima and minima in economic balance problems.

80. Exact Differentials. The total differential of a function is often known as a "complete" or an "exact differential." It has already been shown that the exact differential of the function $u = f(x,y)$ is

$$du = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy \tag{94}$$

where $\partial f / \partial x$ and $\partial f / \partial y$ are in general functions of x and y. It is very common to encounter expressions of the form

$$du = M\,dx + N\,dy \tag{95}$$

in which du is not an exact differential even though M and N are functions of x and y. The necessary and sufficient conditions for du to be an exact differential are easily stated. If du is an exact differential, there must exist a function f of x and y, such that, by comparison of (94) and (95), $\partial f / \partial x = M$ and $\partial f / \partial y = N$. Furthermore, since the order of differentiation is immaterial, it is necessary that

$$\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right) = \frac{\partial M}{\partial y} = \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right) = \frac{\partial N}{\partial x} \tag{96}$$

As an example of the application of this criterion, consider the equation

$$du = 3x^2y\,dx + y^2x\,dy \tag{97}$$

where

$$\frac{\partial M}{\partial y} = \frac{\partial (3x^2y)}{\partial y} = 3x^2 \tag{98}$$

and

$$\frac{\partial N}{\partial x} = \frac{\partial (y^2x)}{\partial x} = y^2 \tag{99}$$

The two derivatives are not equal, and therefore du is not an exact differential; it is impossible to find a function f_1 such that $\partial f / \partial x = 3x^2y$ and $\partial f / \partial y = y^2x$.

On the other hand, in the case of

$$du = 3x^2y^2\,dx + 2x^3y\,dy \tag{100}$$

$\partial M/\partial y = 6x^2y$; and $\partial N/\partial x = 6x^2y$, indicating that du in this case is an exact differential. By the methods of Par. 45, this function is easily determined to be

$$u = x^3y^2 + c \tag{101}*$$

There is a further property relating to exact differentials that is of particular importance in the field of thermodynamics. If Eq. (97) is integrated between limits, we have

$$\int_{u_a}^{u_b} du = u_b - u_a = \int_{x_a}^{x_b} 3x^2y\,dx + \int_{y_a}^{y_b} y^2x\,dy \tag{102}$$

In order to evaluate these integrals, it is necessary to have a functional relation between x and y; *i.e.*, it is necessary to specify the path of the integration.† In general, the value of $(u_b - u_a)$ will depend on the nature of the relation between y and x.

Consider now the integration of (100)

$$\int_{u_a}^{u_b} du = u_b - u_a = \int_{x_a}^{x_b} 3x^2y^2\,dx + \int_{y_a}^{y_b} 2x^3y\,dy \tag{103}$$

Again, it would appear as though the value of $u_b - u_a$ might depend upon the relation between x and y. It will be found, however, that regardless of the nature of the functional relationship chosen between x and y the value of $u_b - u_a$ remains the same. That this must be the case is evident upon reference to (101), where it is seen that

* In the case of an equation in three independent variables

$$du = M\,dx + N\,dy + P\,dz$$

where M, N, and P are functions of x, y, and z, the necessary and sufficient condition that du be an exact differential is that

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}; \qquad \frac{\partial M}{\partial z} = \frac{\partial P}{\partial x}; \qquad \frac{\partial N}{\partial z} = \frac{\partial P}{\partial y}$$

If du is known to be an exact differential, it follows that $u = f(x,y,z)$ and $M = \partial f/\partial x$, $N = \partial f/\partial y$, $P = \partial f/\partial z$.

Similar relations hold for a function of any number of variables.

† Since the path of integration is along some curve, in the plane xy (102) is known in mathematics as a line integral.

$$du = d(x^3y^2) = 3x^2y^2dx + 2x^3y\,dy$$
$$\int_{u_b}^{u_a} du = \int_a^b d(x^3y^2) = x_b^3y_b^2 - x_a^3y_a^2 \tag{104}$$

Evidently, $u_b - u_a$ may be evaluated from (104), in which no functional relation between x and y is involved. Since the value of $\int_{u_b}^{u_a} du$ in (104) depends only upon the limits of the integration or upon the two points x_a, y_a and x_b, y_b, u is said to be a point function or simply a function of x and y, and du is an exact differential.

On the other hand, du in (97) is said to be an inexact differential, because its integral depends not only upon the limits but also upon the path of integration, *i.e.*, upon the nature of the function of x and y.

81. Exact and Inexact Differentials in Thermodynamics. The mathematical principles discussed in Par. 80 are of particular importance in the field of thermodynamics. No attempt will be made at this time to present the refined reasoning employed in the generalization of the results of countless experiments and observations into the first and second laws of thermodynamics, the primary concern of the present discussion being an examination of the mathematical characteristics of the various quantities involved, since these characteristics form the basis of the practical methods of operation employed in any quantitative treatment of the subject.

Let us consider as a system a fixed mass of homogeneous fluid. It is found experimentally that in order to specify the physical state of this system it suffices to fix the values of any two of the quantities pressure, volume, or temperature. Therefore, there is a functional relationship connecting p, v, T, which may be written $T = f(p,v)$ if p and v are taken as independent variables. This functional relationship may be thought of as represented on the pv plane (Fig. 45) where there is a value of T associated with every point in this plane. The differential of T

$$dT = \frac{\partial f}{\partial p}dp + \frac{\partial f}{\partial v}dv \tag{105}$$

is an exact differential. If the system, initially in a physical state represented by point A, changes to state B by any path whatsoever, the temperature at B will be determined solely

from the equation $T_B = f(p_B,v_B)$ and obviously the temperature change $T_B - T_A$ is a function only of the points B and A.

If an attempt be made to determine the work by the system as a result of its increase in volume upon passing from A to B, it is evident that more information is required. Granting reversibility, the pressure-volume work* is represented by the integral $W_{A-B} = \int_{V_A}^{V_B} p\,dv$, which in turn is represented graphically by the area on the p-v diagram under the curve relating p and v during the change of the system from A to B. This curve is known as the "path" along which the change takes place. An infinite number of paths are possible, and the areas beneath these and the v axis are widely different. Since W_{A-B} is not completely determined by the two points representing the initial and final values of p and v, it is clearly incorrect to write $W = f_1(p,v)$, which would denote a functional relationship among W, p, and v. Since W is not a function of p and v, and therefore of no other properties of the system, its differential is not exact.

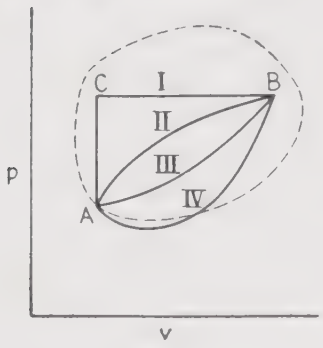

FIG. 45.

Although not readily shown on the p-v diagram, it is found experimentally that the quantity of heat Q crossing the boundary of the system during the state change from A to B is also a function of the path. Therefore, Q cannot be regarded as a function of the coordinates that determine the physical state of the system, and its differential is not exact.

A particularly confusing situation exists with regard to Q as may be seen by considering the following series of changes: Add to a given system a small amount of heat at constant volume dQ_v. Increase the volume at constant temperature by a further addition of heat dQ_T. The total heat added will be

$$dQ = dQ_v + dQ_T.$$

This expression may be transformed by recalling that the heat capacity at constant volume C_v is defined as

* Only pressure-volume work will be considered in this discussion. If other types of work are possible, the equations must be modified by the addition of terms representing this work.

$$C_v = \left(\frac{\partial Q}{\partial T}\right)_v \tag{106}$$

so that $dQ_v = C_v dT = (dQ\ dT)_v dT$ and the latent heat of expansion l_v is defined as

$$l_v = \left(\frac{\partial Q}{\partial v}\right)_T \tag{107}$$

so that $dQ_T = l_v dv = (\partial Q/\partial v)_T dv$.

The total heat added may then be written

$$dQ = \left(\frac{\partial Q}{\partial T}\right)_v dT + \left(\frac{\partial Q}{\partial v}\right)_T dv = C_v dT + l_v dv \tag{108}$$

Equation (108) appears to be similar to the total differential of a function Q of T and v, but the similarity is in appearance only. If dT and dv should be taken along other paths, dQ would, in general, be different; a result corroborated by actual experiment.

Although dQ is not an exact differential, this fact in no way precludes the existence of quantities like C_v and l_v, which are defined as the rate of change of Q with respect to a property of the system along a defined path.

Even though the quantities of heat and work energy associated with the change of state from A to B are both dependent upon the path, it is a remarkable experimental fact that irrespective of the system considered the net amount of heat and work associated with a change from A to B is independent of the path. On the basis that heat evolved is negative and work done by the system is positive, this net amount of heat and work may be written $(Q - W)$. The assertion that the change in the quantity $(Q - W)$ from A to B is determined entirely by the state of the system at A and at B is the equivalent of the statement that the change in $(Q - W)$ is the change in a function completely determined at A and B by the physical properties or coordinates of the system. This point function is known as the "internal energy" E. E is a property of the system, and regardless of the path from A to B, if p and v are selected as the independent variables determining the physical state of the system,

$$\Delta E_{A-B} = (Q - W)_{A-B} = F(p_A,v_A) - F(p_B,v_B) \tag{109}$$

Since E is a function of p and v, its differential

$$dE = dQ - dW = \frac{\partial E}{\partial p} dp + \frac{\partial E}{\partial v} dv \tag{110}$$

is an exact differential, the integral of which from A to B, ΔE_{A-B}, is independent of the path of integration. The first law of thermodynamics, therefore, asserts that the difference of two inexact differentials is an exact differential.

If a cyclical path is described from point A through any region of the pv plane and back to A again (represented by the dotted line in Fig. 45), it is clear that the integral of dE around this cycle may be written

$$\int_{E_A}^{E_A} dE = E_A - E_A = 0 \tag{111}$$

For brevity, an integral of this type is known as a "cyclical integral." The cyclical integral of an exact differential is always equal to zero.

From the second law of thermodynamics, it is possible to deduce the existence of another property of the system known as the "entropy" S. Being a property determined solely by the variables defining the physical state of the system, the change in entropy along a path from A to B is independent of the nature of the path. It may be shown that the change in entropy is most conveniently evaluated along some reversible path from A to B, under which circumstances

$$\Delta S_{A-B} = \int_A^B \frac{dQ_{\text{rev}}}{T} \tag{112}$$

dQ_{rev} being a small quantity of heat crossing the boundary of the system during a reversible process, and T being the absolute temperature.

For a differential change of state along a reversible path, $dS = dQ_{\text{rev}}/T$, and $dQ_{\text{rev}} = T\,dS$. When dQ and dW are replaced in (110) by their values along a reversible path, there is obtained the important differential equation

$$dE = T\,dS - p\,dv \tag{113}$$

which embodies only point functions and exact differentials. When integrated, (113) gives E as a function of the two properties S and V. If this relation is expressed as

$$E = f_E(S,v) \tag{114}$$

it will be seen that

$$dE = \left(\frac{\partial E}{\partial S}\right)_v dS + \left(\frac{\partial E}{\partial v}\right)_S dv \tag{115}$$

and by comparison with (113)

$$\left(\frac{\partial E}{\partial S}\right)_v = T; \qquad \text{and} \qquad \left(\frac{\partial E}{\partial v}\right)_S = -p \tag{116}$$

Apparently, if Eq. (114) is known for a given mass of any homogeneous fluid, it is possible to compute the properties T, p, and E for any physical state of the fluid that may be specified by the independent variables S and v. For this reason, (114) is known as a "fundamental equation" and stands in sharp contrast to the equation of state for the same fluid from which it is impossible to obtain E and S at all temperatures and pressures. The function E is often referred to as a "thermodynamic potential of entropy and volume" since a potential function in mathematics is one that, when known as a function of the independent variables, can be used to determine all the dependent variables.

82. Transformation of Independent Variables in Thermodynamic Systems. Any two of the properties are sufficient to determine the state of the system, and if S and v prove inconvenient it is possible to change, for example, to S and p by introducing a new property H defined in terms of E, p, and v by the equation

$$H = E + pv \tag{117}$$

The differential of H is evidently exact and is

$$dH = dE + p\,dv + v\,dp \tag{118}$$

Substituting for dE its value from (113) gives

$$dH = T\,dS + v\,dp \tag{119}$$

Evidently

$$H = f_H(S,p) \tag{120}$$

and

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp \tag{121}$$

Comparison with (119) indicates that

$$\left(\frac{\partial H}{\partial S}\right)_p = T; \qquad \text{and} \qquad \left(\frac{\partial H}{\partial p}\right)_S = v \tag{122}$$

Equation (120) is another fundamental equation in the sense that once it is known all of the other properties are calculable. The quantity H is known as "enthalpy" or "heat content" and is the thermodynamic potential for entropy and pressure.

This method of changing independent variables by replacing a differential $y\,dx$ with another differential $x\,dy$ by subtracting the differential $d(xy)$ is known in mathematics as a "Lagrangian transformation." It will be noted from (113) that three such transformations are possible in this case: either $p\,dv$ or $T\,dS$ may be replaced separately by $v\,dp$ and $S\,dT$, respectively, or both may be replaced together. This process of change of variable is the origin of the functions H, A, and F.

From a purely practical point of view, it is usually more convenient to select either temperature and volume, or temperature and pressure, as the independent variables. If T and v are selected, we define a new property A in terms of E, T, and S by the equation

$$A = E - TS \tag{123}$$

Differentiating results in

$$dA = dE - T\,dS - S\,dT \tag{124}$$

and substituting for dE from (113) yields

$$dA = -S\,dT - p\,dv \tag{125}$$

A is thus a function of T and v, which may be written

$$A = f_A(T,v) \tag{126}$$

from which

$$dA = \left(\frac{\partial A}{\partial T}\right)_v dT + \left(\frac{\partial A}{\partial v}\right)_T dv \tag{127}$$

Comparison with (125), shows

$$\left(\frac{\partial A}{\partial T}\right)_v = -S; \qquad \text{and} \qquad \left(\frac{\partial A}{\partial v}\right)_T = -p \tag{128}$$

A has been called the "Helmholz free energy" and is evidently the thermodynamic potential for temperature and volume as independent variables.

Finally, if the physical state of the system is to be defined by temperature and pressure, it is possible to define still another function F by the equation

$$F = E - TS + pv \tag{129}$$

the differential of which is

$$dF = dE - T\,dS - S\,dT + p\,dv + v\,dp \tag{130}$$

and when dE is replaced by its value from (113)

$$dF = -S\,dT + v\,dp \tag{131}$$

This last equation shows that F is a function entirely determined by T and p, so that it is permissible to write

$$F = f_F(T,p) \tag{132}$$

and

$$dF = \left(\frac{\partial F}{\partial T}\right)_p dT + \left(\frac{\partial F}{\partial p}\right)_T dp \tag{133}$$

which shows upon comparison with (131) that

$$\left(\frac{\partial F}{\partial T}\right)_p = -S \qquad \text{and} \qquad \left(\frac{\partial F}{\partial p}\right)_T = v \tag{134}$$

F is known as the "free energy" and is the thermodynamic potential for temperature and pressure as independent variables.

83. Relations between the Thermodynamic Functions and Their Derivatives. The thermodynamic functions that have just been defined owe their practical interest to the simplifications they introduce into the calculation of various heat and work effects accompanying the processing of materials. Tables of the numerical values of these functions are of great value, and we shall now examine the methods available for their calculation from quantities that can be measured more directly.

As an example of the general type of procedure, we shall consider a method of calculating the change of internal energy with volume at constant temperature. This necessitates finding the derivative $(\partial E/\partial v)_T$ as a function of v. When E is known at T_A and v_A, it becomes possible to calculate E at T_A and v_B from the equation

$$E_B - E_A = \int_{v_A}^{v_B} \left(\frac{\partial E}{\partial v}\right)_T dv \tag{135}$$

To find $(\partial E/\partial v)_T$ as a function of v, we start with the equation

$$E = f_E(S,v) \tag{136}$$

Since any two variables suffice to determine the state of the system, we note that S is a function of T and v of the general form

$$S = \phi(T,v) \tag{137}$$

If $\phi\,(T,v)$ is substituted for S in (136), E becomes a function of T and v and may be differentiated with respect to v at constant T by the methods of (51). This differentiation gives

$$\left(\frac{\partial E}{\partial v}\right)_T = \left(\frac{\partial E}{\partial S}\right)_v \left(\frac{\partial S}{\partial v}\right)_T + \left(\frac{\partial E}{\partial v}\right)_S \left(\frac{\partial v}{\partial v}\right)_T \tag{138}$$

But $(\partial v/\partial v)_T = 1$, so that

$$\left(\frac{\partial E}{\partial v}\right)_T = \left(\frac{\partial E}{\partial S}\right)_v \left(\frac{\partial S}{\partial v}\right)_T + \left(\frac{\partial E}{\partial v}\right)_S \tag{139}$$

(Note the confusion that would occur here if the subscripts were to be omitted.)

From (116), $(\partial E/\partial S)_v = T$, and $(\partial E/\partial v)_S = -p$. Therefore,

$$\left(\frac{\partial E}{\partial v}\right)_T = T\left(\frac{\partial S}{\partial v}\right)_T - p \tag{140}$$

From (125),

$$dA = -S\,dT - p\,dv$$

and since dA is an exact differential this is of the form of (95) and

$$\left(\frac{\partial S}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v \tag{141}$$

Substituting in (140) gives

$$\left(\frac{\partial E}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p \tag{142}$$

and

$$(E_B - E_A)_T = \int_{v_A}^{v_B} \left[T\left(\frac{\partial p}{\partial T}\right)_v - p \right] dv \tag{143}$$

The derivative $(\partial p/\partial T)_v$ is readily computed from p-v-T data for the substance in question, and the integral is evaluated as the area under a curve of the quantity in brackets vs. v, all quantities being taken at the temperature T. Notice that this calculation holds only for an isothermal change in E. It is impossible from p-v-T data alone to calculate the change of E with T.

As a second example, we shall calculate the change of enthalpy with pressure at constant temperature. Instead of employing

a method similar to that used in deriving (143), we shall start directly with

$$dH = T\,dS + v\,dp \tag{119}$$

Dividing through by dp and imposing the restriction of constant T give

$$\left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T + v \tag{144}$$

But from (131)

$$dF = -S\,dT + v\,dp$$

since dF is an exact differential

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p \tag{145}$$

Substituting in (144) results in

$$\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial v}{\partial T}\right)_p + v \tag{146}$$

The change in enthalpy from a state characterized by T, p_A, to one characterized by T, p_B, is obtained as

$$(H_B - H_A)_T = \int_{p_A}^{p_B}\left[-T\left(\frac{\partial v}{\partial T}\right)_p + v\right]dp \tag{147}$$

Consider now the change of heat capacity with pressure at constant temperature. By definition

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p$$

But dQ may be replaced by $T\,dS$ to give

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p$$

and

$$\left(\frac{\partial C_p}{\partial p}\right)_T = T\frac{\partial}{\partial p}\left[\left(\frac{\partial S}{\partial T}\right)_p\right]_T \tag{148}$$

Now S is itself a function of p and T, and the order of differentiation of the second partial derivatives is immaterial so that we may write

$$T\frac{\partial}{\partial p}\left[\left(\frac{\partial S}{\partial T}\right)_p\right]_T = T\frac{\partial}{\partial T}\left[\left(\frac{\partial S}{\partial p}\right)_T\right]_p \tag{149}$$

Substituting for $(\partial S/\partial p)_T$ from (145) yields

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T\frac{\partial}{\partial T}\left(\frac{\partial v}{\partial T}\right)_p = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_p \tag{150}$$

and

$$[(C_p)_{p_B} - (C_p)_{p_A}]_T = -\int_{p_A}^{p_B} T\left(\frac{\partial^2 v}{\partial T^2}\right)_p dp \tag{151}$$

p-v-T data are sufficient for evaluating the derivative $\partial^2 v\ \partial T^2$, but if these data are known only in the form of tables great care must be taken in performing the two necessary differentiations if the final result is to have reasonable accuracy.

That the three examples which have just been solved are typical of the simpler cases which may arise becomes evident on consideration of the following problem:

Determine an expression for the change of internal energy with volume at constant enthalpy $(\partial E\ \partial v)_H$ in terms of the variables p, T, v, C_p and the readily obtainable derivatives $(\partial v\ \partial T)_p$ and $(\partial v\ \partial p)_T$. It may be judged by the result on page 176 that in the absence of a general systematic method of attack, this problem would lead to a lengthy and involved analysis. Fortunately, systematic methods of such simplicity have been devised that solution of this type of problem may be reduced to a standard procedure.

84. Systematic Derivation of Relations among the First Partial Derivatives of the Thermodynamic Quantities. Ten important thermodynamic quantities, *viz.*, p, v, T, S, E, H, A, F, Q, and W have been encountered in the preceding paragraphs. The heat capacities C_p and C_v are not included since they are by definition derivatives involving the fundamental quantities. Three quantities are involved in each derivative of the form $(\partial y/\partial x)_z$ where x, y, and z refer to any three of p, v, T, etc.

Since there are 10 choices for y, 9 choices for x, and 8 choices for z, the total number of first derivatives is $10 \times 9 \times 8 = 720$. The fact that any one of these quantities (except Q and W) may be expressed as a function of any two others, coupled with the additional relations due to their properties as point functions, makes it possible to express any one of these 720 derivatives as a function of three others and certain of the fundamental quantities. The theory of combinations shows that there are over 11 million such relations possible. It is neither necessary

nor desirable that all these relations be listed, but it is extremely valuable to have available a method whereby any one of them may be formulated promptly.

One method of deriving these relations has been devised by Bridgman.* In this method, the general derivative $(\partial y\ \partial x)_z$ is, in a purely formal fashion, written in the form $(\partial y)_z\ (\partial x)_z$. This is possible because of the mathematical identity

$$\left(\frac{\partial y}{\partial x}\right)_z = \frac{(\partial y/\partial \alpha)_z}{(\partial x/\partial \alpha)_z} \tag{152}$$

which follows from the two equations

$$dy = \left(\frac{\partial y}{\partial \alpha}\right)d\alpha + \left(\frac{\partial y}{\partial z}\right)dz \tag{153}$$

$$dx = \left(\frac{\partial x}{\partial \alpha}\right)d\alpha + \left(\frac{\partial x}{\partial z}\right)dz \tag{154}$$

At constant z, $dz = 0$, and (152) is the ratio of the two equations. It is not necessary that y and x be exact differentials, for it will be recalled from Par. 81 that expressions such as (153) and (154) are quite possible even though it may not be permissible to write $y = f_1(\alpha,z)$ and $x = f_2(\alpha,z)$. Therefore, y and x can represent Q and W as well as any of the other fundamental quantities.

If $(\partial y\ \partial \alpha)_z$ and $(\partial x\ \partial \alpha)_z$, two finite quantities, be denoted by $(\partial y)_z$ and $(\partial x)_z$, the ratio of these two quantities will, of course, be $(\partial y\ \partial x)_z$. It must be noted that $(\partial y)_z$ and $(\partial x)_z$ are not equal to $(\partial y\ \partial \alpha)_z$ and $(\partial x\ \partial \alpha)_z$ but that these are merely symbols of notation which give the correct result for the quantity they denote when written in ratio form.

Bridgman presents tables of $(\partial y)_z$ and $(\partial x)_z$ (x,y, and z being any of the 10 fundamental quantities) in terms of various important reference derivatives and certain of the 10 quantities.† These tables reduce the problem of determining any derivative of the form $(\partial y/\partial x)_z$ to a purely mechanical operation. In spite of their simplicity and value, however, they are limited in scope, and it is possible to present the whole subject from a much broader point of view in a much more compact form.

* *Phys. Rev.*, II, **3**, 273 (1914).

† BRIDGMAN, P. W., "Condensed Collection of Thermodynamic Formulas," Harvard University Press, Cambridge, Mass., 1926.

The basic principles of the method now to be described have been discussed in several of the older texts on thermodynamics,* but their complete systematization into a remarkably compact and usable form has been effected by Shaw.†

Although an appreciation of the theory underlying the method is not essential to its practical use, the theory provides an instructive example of the increased analytical power that may result from a proper choice of notation. The condensed and systematized notation for manipulating partial derivatives involves mathematical quantities known as "Jacobians," the properties of which will now be discussed.

85. Partial Derivatives in Jacobian Notation. A Jacobian is a determinant whose elements are certain partial derivatives. A second-order determinant is a quantity consisting of four elements in square array and defined by the identical equation

$$\begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - bc \tag{155}$$

The determinant

$$\begin{vmatrix} \left(\frac{\partial u}{\partial x}\right)_y & \left(\frac{\partial u}{\partial y}\right)_x \\ \left(\frac{\partial v}{\partial x}\right)_y & \left(\frac{\partial v}{\partial y}\right)_x \end{vmatrix} = \left(\frac{\partial u}{\partial x}\right)_y \cdot \left(\frac{\partial v}{\partial y}\right)_x - \left(\frac{\partial u}{\partial y}\right)_x \cdot \left(\frac{\partial v}{\partial x}\right)_y \tag{156}$$

is called the "Jacobian of u and v with respect to x and y" and is denoted by the symbols $\partial(u,v)/\partial(x,y)$, or $J(u,v\ x,y)$. The order of the terms of the Jacobian is important, for it will be seen that interchanging the order of any two terms changes the sign. It is easily shown that

$$\frac{\partial(u,v)}{\partial(x,y)} = -\frac{\partial(v,u)}{\partial(x,y)} = \frac{\partial(v,u)}{\partial(y,x)} = -\frac{\partial(u,v)}{\partial(y,x)} \tag{157}$$

It is also clear that

$$\frac{\partial(u,u)}{\partial(x,y)} = 0 \tag{158}$$

The general partial derivative $(\partial y/\partial x)_z$ is equivalent to the Jacobian $\partial(y,z)/\partial(x,z)$, because by definition

* See BRYAN, "Thermodynamics," B. G. Teubner, Leipzig, 1907.

† SHAW, A. N., *Phil. Trans. Roy. Soc.*, **A234**, 299–328 (1935).

$$\frac{\partial(y,z)}{\partial(x,z)} = \begin{vmatrix} \left(\frac{\partial y}{\partial x}\right)_z & \left(\frac{\partial y}{\partial z}\right)_x \\ \left(\frac{\partial z}{\partial x}\right)_z & \left(\frac{\partial z}{\partial z}\right)_x \end{vmatrix} = \left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial z}{\partial z}\right)_x - \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_z$$

But $(\partial z/\partial z)_x = 1$, and $(\partial z/\partial x)_z = 0$, so that

$$\left(\frac{\partial y}{\partial x}\right)_z = \frac{\partial(y,z)}{\partial(x,z)}$$

It is possible to expand $(\partial y/\partial x)_z$ into two Jacobians involving two new variables α and β, provided that it is possible to write the equations

$$dy = \left(\frac{\partial y}{\partial \alpha}\right)_\beta d\alpha + \left(\frac{\partial y}{\partial \beta}\right)_\alpha d\beta \tag{159}$$

$$dx = \left(\frac{\partial x}{\partial \alpha}\right)_\beta d\alpha + \left(\frac{\partial x}{\partial \beta}\right)_\alpha d\beta \tag{160}$$

$$dz = \left(\frac{\partial z}{\partial \alpha}\right)_\beta d\alpha + \left(\frac{\partial z}{\partial \beta}\right)_\alpha d\beta \tag{161}$$

dy, dx, and dz are merely variations in the quantities y, x, and z, and no assumption is made as to their being functions of α and β or* exact differentials, although this may often be the case in thermodynamics, where y, for instance, might stand for v, and α and β for p and T. With z held constant so that $dz = 0$, (159) and (161) will be solved for $d\alpha$. The solution in determinate form is

$$d\alpha = \frac{\begin{vmatrix} dy & \left(\frac{\partial y}{\partial \beta}\right)_\alpha \\ 0 & \left(\frac{\partial z}{\partial \beta}\right)_\alpha \end{vmatrix}}{\begin{vmatrix} \left(\frac{\partial y}{\partial \alpha}\right)_\beta & \left(\frac{\partial y}{\partial \beta}\right)_\alpha \\ \left(\frac{\partial z}{\partial \alpha}\right)_\beta & \left(\frac{\partial z}{\partial \beta}\right)_\alpha \end{vmatrix}} = \frac{\left(\frac{\partial z}{\partial \beta}\right)_\alpha dy}{\frac{\partial(y,z)}{\partial(\alpha,\beta)}} \tag{162}$$

With z still constant, (160) and (161) may be solved for $d\alpha$ in similar fashion to give

$$d\alpha = \frac{\left(\frac{\partial z}{\partial \beta}\right)_\alpha dx}{\frac{\partial(x,z)}{\partial(\alpha,\beta)}}$$

* See Par. 81.

Elimination of $d\alpha$ between these two equations gives

$$\frac{dy}{\dfrac{\partial(y,z)}{\partial(\alpha,\beta)}} = \frac{dx}{\dfrac{\partial(x,z)}{\partial(\alpha,\beta)}} \tag{163}$$

and since z has been held constant

$$\left(\frac{\partial y}{\partial x}\right)_z = \frac{\partial(y,z)}{\partial(x,z)} = \frac{\dfrac{\partial(y,z)}{\partial(\alpha,\beta)}}{\dfrac{\partial(x,z)}{\partial(\alpha,\beta)}} = \frac{\left(\dfrac{\partial y}{\partial \alpha}\right)_\beta \left(\dfrac{\partial z}{\partial \beta}\right)_\alpha - \left(\dfrac{\partial z}{\partial \alpha}\right)_\beta \left(\dfrac{\partial y}{\partial \beta}\right)_\alpha}{\left(\dfrac{\partial x}{\partial \alpha}\right)_\beta \left(\dfrac{\partial z}{\partial \beta}\right)_\alpha - \left(\dfrac{\partial z}{\partial \alpha}\right)_\beta \left(\dfrac{\partial x}{\partial \beta}\right)_\alpha} \tag{164}$$

As an example of the simplification (164) effects in the proof of many important relations, consider its use in evaluating the group $(\partial y\ \partial x)_z \cdot (\partial x\ \partial z)_y \cdot (\partial z\ \partial y)_x$. When $\partial(y,x)/\partial(\alpha,\beta)$ is denoted by $J(y,x)$, the derivatives in this group become, by (164), $J(y,z)/J(x,z) \cdot J(x,y)\ J(z,y) \cdot J(z,x)/J(y,x)$. Since $J(y,z) = -J(z,y)$, $J(x,z) = -J(z,x)$, and $J(x,y) = -J(y,x)$, simple cancellation shows that the result is (-1) as found in Par. 78 by another method.

Another relation of importance arises from division of

$$dE = T\,dS - p\,dv$$

by dx at constant y (x and y being any of the thermodynamic variables) to give

$$\left(\frac{\partial E}{\partial x}\right)_y = T\left(\frac{\partial S}{\partial x}\right)_y - p\left(\frac{\partial v}{\partial x}\right)_y \tag{165}$$

In terms of Jacobian notation, (165) may be written

$$\frac{J(E,y)}{J(x,y)} = \frac{TJ(S,y)}{J(x,y)} - p\frac{J(v,y)}{J(x,y)} \tag{166}$$

which reduces to

$$J(E,y) = TJ(S,y) - pJ(v,y)$$

The relation

$$\left(\frac{\partial T}{\partial v}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_v \tag{167}$$

arising from dE being an exact differential may be written as

$$\frac{J(T,S)}{J(v,S)} = -\frac{J(p,v)}{J(S,v)} \tag{168}$$

and since $J(S,v) = -J(v,S)$ this reduces to

$$J(T,S) = J(p,v) \tag{169}$$

an equation much easier to remember than (167) and one from which it is possible to derive any of the Maxwell relations (167), (141), (145) merely by placing α and β equal to (S,v), (T,v), and (T,p), respectively.

Another relation of importance in the construction of Table XIV described in a later paragraph comes from an equation of the familiar form

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \tag{170}$$

which by (164) may be written as

$$dz = \frac{J(z,y)}{J(x,y)}dx + \frac{J(z,x)}{J(y,x)}dy \tag{171}$$

or

$$J(x,y)dz + J(y,z)dx + J(z,x)dy = 0 \tag{172}$$

provided that x, y, and z are related to α and β by equations of the type of (159), (160), and (161).

If u and w are two more variables related to α and β in the same manner, (172) may be divided by du at constant w to give

$$J(x,y)\left(\frac{\partial z}{\partial u}\right)_w + J(y,z)\left(\frac{\partial x}{\partial u}\right)_w + J(z,x)\left(\frac{\partial y}{\partial u}\right)_w = 0 \tag{173}$$

When these derivatives are expressed in the form of Jacobians as permitted by (164), this last equation becomes

$$J(x,y)J(z,w) + J(y,z)J(x,w) + J(z,x)J(y,w) = 0 \tag{174}$$

If $x = p$, $y = v$, $z = T$, and $w = S$, (174) gives the important relation

$$J(p,v)J(T,S) + J(v,T)J(p,S) + J(T,p)J(v,S) = 0 \tag{175}$$

where the independent variables α and β associated with the Jacobians may be any two of the thermodynamic quantities.

The important equation (164) makes possible a systematic solution to the problem proposed on page 170. Since the solution is to be in terms of C_p, $(\partial v/\partial p)_T$ and $(\partial v/\partial T)_p$, we take p and T as independent variables, *i.e.*, $p = \alpha$, $T = \beta$, in (164). Then

$$\left(\frac{\partial E}{\partial v}\right)_H = \frac{(\partial E/\partial p)_T(\partial H/\partial T)_p - (\partial H/\partial p)_T(\partial E/\partial T)_p}{(\partial v/\partial p)_T(\partial H/\partial T)_p - (\partial H/\partial p)_T(\partial v/\partial T)_p} \quad (176)$$

From (146), $(\partial H/\partial p)_T = -T(\partial v/\partial T)_p + v$, and from the definition of C_p and H, combined with the first law,

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p$$

From (113),

$$dE = T\,dS - p\,dv$$

$$\left(\frac{\partial E}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p - p\left(\frac{\partial v}{\partial T}\right)_p \quad (177)$$

But from $dQ = T\,dS$, it is clear that $(\partial Q/\partial T)_p = C_p = T(\partial S/\partial T)_p$ and

$$\left(\frac{\partial E}{\partial T}\right)_p = C_p - p\left(\frac{\partial v}{\partial T}\right)_p \quad (178)$$

The only quantity in (176) that is not now in the required terms is $(\partial E/\partial p)_T$. This is obtained from (113) after division by dp, and is

$$\left(\frac{\partial E}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T - p\left(\frac{\partial v}{\partial p}\right)_T$$

which becomes, after substitution for $(\partial S/\partial p)_T$ from (145),

$$\left(\frac{\partial E}{\partial p}\right)_T = -T\left(\frac{\partial v}{\partial T}\right)_p - p\left(\frac{\partial v}{\partial p}\right)_T \quad (179)$$

By replacing the quantities in (176) by their equivalents in terms of the desired derivatives, we obtain

$$\left(\frac{\partial E}{\partial v}\right)_H = \frac{[-T(\partial v/\partial T)_p - p(\partial v/\partial p)_T]C_p - [-T(\partial v/\partial T)_p + v][C_p - p(\partial v/\partial T)_p]}{(\partial v/\partial p)_T C_p - [-T(\partial v/\partial T)_p + v](\partial v/\partial T)_p} \quad (180)$$

Upon expansion of terms, this becomes

$$\left(\frac{\partial E}{\partial v}\right)_H = \frac{pv(\partial v/\partial T)_p - v(p - p(p(\partial v/\partial p)_T - pT(\partial v/\partial T)_p^2}{C_p(\partial v/\partial p)_T + T(\partial v/\partial T)_p^2 - v(\partial v/\partial T)_p} \quad (181)$$

a result of sufficient complication to indicate the power of this method of attack.

86. The Construction and Use of Simple Tables for Deriving Any of the Relations among the Fundamental Thermodynamic Quantities and Their Partial Derivatives. Even though it is essentially systematic, the method just employed in the derivation of Eq. (181) is quite time consuming and requires some experience with the general thermodynamic equations. Fortunately, the procedure incident to such derivations has been abbreviated still further by means of a simple table due to Shaw.* Although Table XIV owes its compact form to the use of Jacobians, and therefore requires some knowledge of the properties of Jacobians for its construction, experience has shown that its practical use follows immediately from a few simple examples. Following the explanation of its construction, the practical use of the table will be demonstrated by examples.

Table XIV lists values for $J(x,y)$ in terms of one or more of P, V, T, and S, and the Jacobians

$$\left.\begin{aligned} J(v,T) &= -J(T,v) = a \\ J(p,v) &= J(T,S) = -J(v,p) = -J(S,T) = b \\ J(p,S) &= -J(S,p) = c \\ J(p,T) &= -J(T,p) = l \\ J(v,S) &= -J(S,v) = n \end{aligned}\right\} \tag{182}$$

In terms of the letters, (175) becomes simply

$$b^2 + ac - ln = 0 \tag{183}$$

The value of $J(x,y)$ is found at the intersection of row x and column y. The upper left-hand corner of Table XIV may be filled immediately from the definitions (182). The lower left-hand corner follows by visualizing the expressions for dE (113), dH (119), dA (125), dF (131), dQ, and dW in Jacobian form. For example, $dH = T\,dS + v\,dp$ becomes

$$J(H,y) = TJ(S,y) + vJ(p,y)$$

where y might be any permissible variable. When $y = T$, we have $J(H,T) = TJ(S,T) + vJ(p,T) = -Tb + vl$. Similarly, $dQ = T\,dS$, and $J(Q,p) = TJ(S,p) = -Tc$. The upper right-hand portion of the table is obtained from the lower left merely by reversal of signs, and the lower right is obtained by a repetition of the process just described. Only half of the lower right

* SHAW, *loc. cit.*

TABLE XIV.—VALUES OF $J(x,y)$

$$J(x,y) = \left(\frac{\partial x}{\partial \alpha}\right)_\beta \left(\frac{\partial y}{\partial \beta}\right)_\alpha - \left(\frac{\partial x}{\partial \beta}\right)_\alpha \left(\frac{\partial y}{\partial \alpha}\right)_\beta; \qquad b^2 + ac - ln = 0$$

$y \rightarrow$ x $\downarrow$	p	v	T	S	E	H	A	F	Q	W
p	0	b	l	c	$Tc - pb$	Tc	$-Sl - pb$	$-Sl$	Tc	pb
v	$-b$	0	a	n	Tn	$Tn - vb$	$-Sa$	$-Sa - vb$	Tn	0
T	$-l$	$-a$	0	b	$Tb + pa$	$Tb - vl$	pa	$-vl$	Tb	$-pa$
S	$-c$	$-n$	$-b$	0	pn	$-vc$	$Sb + pn$	$Sb - vc$	0	$-pn$
E	$-Tc + pb$	$-Tn$	$-Tb - pa$	$-pn$	0	$-Tvc$	$T(Sb + pn)$	$T(Sb - vc)$	$-pTn$	$-Tpn$
						$-p(Tn - vb)$	$+pSa$	$-p(Sa + vb)$		
H	$-Tc$	$-Tn + vb$	$-Tb + vl$	vc	Tpn	0	$T(St + pn)$	$T(Sb - vc)$	vTC	$-Tpn$
					$+v(Tc - pb)$		$-v(Sl + pv)$	$-vSl$		$+vpb$
A	$Sl + pv$	Sa	$-pa$	$-Sb - pn$	$-T(Sb + pn)$	$-T(Sb + pn)$	0	Svl	$-STb - pTn$	$-Spa$
					$-pSa$	$+v(Sl - pv)$		$+p(Sa + vb)$		
F	Sl	$Sa + vb$	vl	$-Sb + vc$	$-T(Sb - vc)$	$-T(Sb - vc)$	$-Svl$	0	$-Stb + vTc$	$-Spa + vpb$
					$+p(Sa + vb)$	$+vSl$	$-p(Sa + bv)$			
Q	$-Tc$	$-Tn$	$-Tb$	0	pTn	$-vTc$	$STb + pTn$	$sTb - vTc$	0	$-Tpn$
W	$-pb$	0	pa	pn	Tpn	$Tpn - vpb$	$-Spa$	$-Spa - vpb$	Tpn	0

demands any work, the other half being obtained by reversal of signs. For example, to obtain $J(A,F)$ we write

$$dA = -S\,dT - p\,dv$$

in the Jacobian form. $J(A,F) = -SJ(T,F) - pJ(v,F)$; $J(T,F)$ and $J(v,F)$ are immediately obtainable from the upper right-hand section already filled in.

The utility of Table XIV will be illustrated by means of several examples that have been solved by other methods.

Example I. Evaluate $(\partial H/\partial p)_T$ in terms of derivatives involving p and T as independent variables. First express $(\partial H/\partial p)_T$ in Jacobian notation

$$\left(\frac{\partial H}{\partial p}\right)_T = \frac{J(H,T)}{J(p,T)} \tag{184}$$

Substitute for the Jacobians their values read from Table XIV.

$$\frac{J(H,T)}{J(p,T)} = \frac{-Tb + vl}{l} = \frac{-Tb}{l} + v \tag{185}$$

Either from the table or from (182), it is seen that $b = J(p,v)$ and $l = J(p,T)$. Therefore,

$$\left(\frac{\partial H}{\partial p}\right)_T = -\frac{TJ(p,v)}{J(p,T)} + v$$

But $J(p,v)/J(p,T) = (\partial v/\partial T)_p$ by (164) so that

$$\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial v}{\partial T}\right)_p + v \tag{146}$$

Example II: Transform $(\partial H/\partial p)_T$ into groups of derivatives in which the two independent variables are selected in turn from the group p, v, T, and S. In general, it is possible to express any derivative in terms of three others containing the desired independent variables. From (185) and

$$b^2 + ac - ln = 0$$

$$\left(\frac{\partial H}{\partial p}\right)_T = \frac{-Tb}{l} + v = \frac{-Tbn}{b^2 + ac} + v \tag{186}$$

The desired expressions may now be read off directly from (186) and Table XIV. Take the case where v and S are independent.

$$\left(\frac{\partial H}{\partial p}\right)_T = \frac{-TJ(p,v)J(v,S)}{J(p,v)^2 + J(v,T)J(p,S)} + v \tag{187}$$

Since $\alpha = v$ and $\beta = S$,

$$J(p,v) = \frac{\partial(p,v)}{\partial(v,S)} = -\left(\frac{\partial p}{\partial S}\right)_v; \qquad J(v,S) = \frac{\partial(v,S)}{\partial(v,S)} = 1$$

$$J(v,T) = \frac{\partial(v,T)}{\partial(v,S)} = \left(\frac{\partial T}{\partial S}\right)_v; \qquad J(p,S) = \frac{\partial(p,S)}{\partial(v,S)} = \left(\frac{\partial p}{\partial v}\right)_S$$

Substitution of these values into (187) gives the required result.

$$\left(\frac{\partial H}{\partial p}\right)_T = \frac{-T(\partial p/\partial S)_v + v(\partial p/\partial S)_v^2 + v(\partial T/\partial S)_v(\partial p/\partial v)_S}{(\partial p/\partial S)_v^2 + (\partial T/\partial S)_v(\partial p/\partial v)_S}$$

In this case, it was wise to avoid using the first expression in (186) containing b/l, because $l = J(p,T) = \partial(p,T)/\partial(v,S)$ when v and S are independent, and since this will not reduce to one partial derivative the final expression would obtain four partial derivatives, one more than is really necessary.

Example III. What relation exists among the Joule-Thomson coefficient $\mu_H = (\partial T/\partial p)_H$, the heat capacity at constant pressure C_p, and the derivative $(\partial H/\partial p)_T = \phi_H$?

From Table XIV,

$$\mu_H = \left(\frac{\partial T}{\partial p}\right)_H = \frac{J(T,H)}{J(p,H)} = \frac{Tb - vl}{Tc}$$

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p = \frac{J(Q,p)}{J(T,p)} = \frac{-Tc}{-l}$$

$$\phi_H = \left(\frac{\partial H}{\partial p}\right)_T = \frac{J(H,T)}{J(p,T)} = \frac{-Tb + vl}{l}$$

Inspection immediately reveals the important relation

$$C_p = -\frac{\phi_H}{\mu_H}$$

Example IV. Using Table XIV, evaluate $(\partial E/\partial v)_H$ in terms of the minimum number of derivatives involving p and T as independent variables.

$$\left(\frac{\partial E}{\partial v}\right)_H = \frac{J(E,H)}{J(v,H)} = \frac{-Tvc - p(Tn - vb)}{Tn - vb}$$

$$= \frac{-TvJ(p,S) - pTJ(v,S) + pvJ(p,v)}{TJ(v,S) - vJ(p,v)} \tag{188}$$

Each Jacobian in this expression reduces to one derivative when $\alpha = p, \beta = T$ except $n = J(v,S)$ which, upon expansion, involves four derivatives. It is possible to avoid these four by using the

relation $b^2 + ac - ln = 0$. The choice of p and T as α and β makes $l = J(p,T) = 1$, and

$$n = b^2 + ac = J(p,v)^2 + J(v,T)J(p,S).$$

Substituting in (188) gives

$$\left(\frac{\partial E}{\partial v}\right)_H = \frac{-TvJ(p,S) - pTJ(p,v)^2 - pTJ(v,T)J(p,S) + pvJ(p,v)}{TJ(p,v)^2 + TJ(v,T)J(p,S) - vJ(p,v)} \tag{189}$$

But

$$J(p,S) = \frac{\partial(p,S)}{\partial(p,T)} = \left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}$$

$$J(p,v) = \frac{\partial(p,v)}{\partial(p,T)} = \left(\frac{\partial v}{\partial T}\right)_p$$

$$J(v,T) = \frac{\partial(v,T)}{\partial(p,T)} = \left(\frac{\partial v}{\partial p}\right)_T$$

Substituting these derivatives into (189) gives a final equation identical with (181).

Example V. Quite frequently it may be desirable to express a derivative in terms of several other derivatives that have been more accurately measured, but that do not involve the same independent variables. The customary methods of derivation lead to long and involved analyses in problems of this nature, and the simplicity of the present method is well illustrated by the ease with which one of the more complicated expressions is developed. It is required to find an expression for the variation of fugacity f with temperature at constant enthalpy, in terms of the derivatives Cp, $(\partial H/\partial p)_T$, and the fundamental quantities.

Since fugacity is not listed directly in Table XIV, we obtain from its definition

$$dF = RT\, d\log_e f$$

the equation

$$\left(\frac{\partial \log_e f}{\partial T}\right)_H = \frac{1}{RT}\left(\frac{\partial F}{\partial T}\right)_H \tag{190}$$

and $(\partial F/\partial T)_H$ may be evaluated from the table in terms of the desired derivatives

$$\left(\frac{\partial F}{\partial T}\right)_H = \frac{J(F,H)}{J(T,H)} = \frac{-T(Sb - vc) + vSl}{Tb - vl} \tag{191}$$

As found in Example III,

$$C_p = \frac{Tc}{l}; \qquad c = \frac{C_p l}{T} \tag{192}$$

$$\left(\frac{\partial H}{\partial p}\right)_T = \phi_H = \frac{-Tb + vl}{l}; \qquad b = \frac{l(v - \phi_H)}{T}$$

Substituting in (190) and (191) gives

$$\left(\frac{\partial \log_e f}{\partial T}\right)_H = \frac{-S(v - \phi_H) + vC_p + vS}{-\phi_H RT} \tag{193}$$

Table XIV is particularly useful in answering such questions as the following: Is it possible to find an expression for the variation of free energy with temperature, not involving the entropy S, by holding any of the 10 fundamental quantities constant? Looking across the row of expressions for F, it is seen at once that such an expression is impossible, at least in terms of first derivatives, since the only column in which S is absent (excluding zero) is the T column itself.

Example VI. In many cases, the equation of state is available, and additional relations are easily derived. For example: What is the Joule-Thomson coefficient for a perfect gas with equation of state $pv = RT$?

$$\mu_H = \frac{Tb - vl}{Tc}$$

If $\alpha = p$ and $\beta = T$, $b = J(p,v) = (\partial v/\partial T)_p = R/p$, then $l = J(p,T) = 1$. Therefore $\mu_H = 0$.

Obtain an expression for μ_H when the equation of state is $PV = CRT$, C being an empirical compressibility factor, which is a function of the temperature and pressure. In this case

$$b = \left(\frac{\partial v}{\partial T}\right)_p = \frac{CR}{p} + \frac{RT}{p}\left(\frac{\partial C}{\partial T}\right)_p; \qquad l = 1;$$

$$c = J(p,S) = \left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}$$

Therefore,

$$\mu_H = \frac{T\left[\frac{CR}{p} + \frac{RT}{p}\left(\frac{\partial C}{\partial T}\right)_p\right] - v}{C_p} \tag{194}$$

The methods described may be extended for use in the treatment of second partial derivatives, as described in detail by Shaw.*

* *Loc. cit.*

CHAPTER V

INFINITE SERIES

87. Use of Series. Infinite series of various types find wide and varied applications in engineering calculations. The result of natural processes is frequently best expressed by such a series, and the use of the series form of expression is frequently convenient for subsequent mathematical operations, even though an alternative expression involving a single term is available. Series are of value in the solution of ordinary differential equations and are of fundamental importance in the solution of partial differential equations.

As an example, consider the washing of soda pulp in successive steps, using fresh water each time. The original pulp contains a lb. water with x_0 lb. dissolved salts per lb. water. In each washing, b lb. of water are used, the pulp and water being well agitated together. After agitation, the solution is drained off, leaving a lb. of water in the pulp, as at the start. If x_n represents the concentration of the solution at the end of the nth wash, as pounds solute per pound water, then

$$ax_0 = ax_1 + bx_1$$

or

$$x_1 = \left(\frac{a}{a+b}\right)x_0$$

and

$$x_n = \left(\frac{a}{a+b}\right)^n x_0$$

The total amount of solute recovered in the wash water is $bx_1 + bx_2 + bx_3 + \cdots bx_n =$

$$\left[\frac{a}{a+b} + \left(\frac{a}{a+b}\right)^2 + \cdots \left(\frac{a}{a+b}\right)^n\right]bx_0 \quad (1)$$

The recovery is obviously a function a $(a + b)$. If five washings are used, the recovery is represented by a "polynomial of the fifth degree" since the exponent on the last term is 5. This is a "finite series."

As the washing is continued indefinitely, the solute remaining in the pulp approaches zero as a limit as n approaches infinity, and the resulting series may be equated to the original solute content of the pulp.

$$ax_0 = \left[\frac{a}{a+b} + \left(\frac{a}{a+b}\right)^2 + \left(\frac{a}{a+b}\right)^3 + \cdots\right] bx_0$$

$$= bx_0 \sum_{n=1}^{n=\infty} \left(\frac{a}{a+b}\right)^n \tag{2}$$

This is an "infinite series." Since, in this case, a and b are always positive numbers, $a/(a+b)$ is always a fraction, and $[a/(a+b)]^n$ gets smaller and smaller as n increases. The sum of the terms approaches the perfectly definite value a/b as n approaches infinity, and the series is said to "converge."

88. Convergence. An infinite series similar in form to (2) is

$$y = \frac{1}{1-x} = 1 + x + x^2 + x^3 + \cdots = \sum_{n=0}^{n=\infty} x^n \tag{3}$$

which may be obtained by algebraic division of unity by $1 - x$. If $x = \frac{1}{2}$, this reduces to

$$2 = 1 + \tfrac{1}{2} + \tfrac{1}{4} + \tfrac{1}{8} + \cdots \tag{4}$$

which is correct. If x is 2, the result is

$$-1 = 1 + 2 + 4 + 8 + \cdots \tag{5}$$

which obviously is not correct unless the terms become negative at large values of n. Similarly, when x is -1, the result is

$$\tfrac{1}{2} = 1 - 1 + 1 - 1 + 1 - 1 + \cdots \tag{6}$$

which is also incorrect.

If infinite series are to be used, it is clearly of importance to know when they are going to give ridiculous results, as in (5) and (6). There is usually no way of checking the validity of a summation by inspection, as was possible in the preceding examples, and it is necessary to have independent means of finding out whether the series does or does not approach a finite limit as n approaches infinity. Such tests are called "convergence tests." The series (4) is said to "converge,"

series (5) "diverges," and (6) "oscillates." Fortunately, the series encountered in practice usually converge, but it is possible to have a series in which the terms appear to become negligible by about the fifth or sixth term and yet have large and increasing terms as n reaches 15 or 20.

A useful test for convergence is the so-called "ratio test." If the ratio of the $(n + 1)$th term to the nth term approaches a definite fraction less than unity as n approaches infinity, then the series converges. In series (3), the ratio of the $(n + 1)$th to the nth term is x. Thus the series converges if x is numerically less than 1. If the ratio obtained is greater than 1, the series diverges; if the ratio is 1, the test is inconclusive.

Other tests sometimes used are the "comparison tests." The series tested is compared term by term with a series whose convergence or divergence has been established. If every term of the series tested is less than the corresponding term of a known convergent series, the series in question is also convergent. By comparison with (4), it is apparent that the series

$$1 + \tfrac{1}{3} + \tfrac{1}{5} + \tfrac{1}{9} + \tfrac{1}{17} + \cdots$$

is convergent. The fact that the two first terms are the same does not matter, for they may be omitted from the series compared. If every term of a series is greater than a series known to be divergent, it is also divergent.

It should be noted that a series of terms in x may be divergent or convergent depending on the value of x that is substituted. The range of values of x for which the series converges is termed the "region of convergence." Thus series (3) converges in the region $x = -1$ to $x = +1$.

89. Power Series. The power series

$$f(x) = a_0 + a_1x + a_2x^2 + a_3x^3 + \cdots \tag{7}$$

is of particular practical importance. Functions may usually be expressed ("expanded") in power series, and experimental results may be represented approximately by a polynomial (Chap. VII) or an infinite power series. In general, a power series represents a continuous function of x in the region of convergence of the series.

Applying the ratio test for convergence, we note that the power series (7) converges if the ratio $a_nx^n/a_{n-1}x^{n-1}$ of the $(n + 1)$th

term to the nth term approaches a definite fraction as n increases indefinitely. If $a_n a_{n-1}$ approaches a limit F, then Fx must be a fraction if the series is to converge, *i.e.*, Fx must be less than unity. This will be true provided that x is greater than $-1/F$ and less than $1/F$. It follows that the *region of convergence* of the series (7) is from $x = -(1/F)$ to $x = +(1/F)$. It may or may not converge at $x = -(1/F)$ and $x = +(1/F)$.

It may be shown that two power series may be added, subtracted, divided, or multiplied. Other operations may be performed on power series that may be performed with ordinary polynomials, and the resulting series will converge if the series treated converge. For example, if

$$y = a_0 + a_1x + a_2x^2 + a_3x^3 + \cdots \tag{8}$$

then

$$y^2 = a_0^2 + 2a_0a_1x + (2a_0a_2 + a_1^2)x^2 + (2a_0a_3 + 2a_1a_2)x^3 + (2a_0a_4 + 2a_1a_3 + a_2^2)x^4 + (2a_0a_5 + 2a_1a_4 + 2a_2a_3)x^5 + (2a_0a_6 + 2a_1a_5 + 2a_2a_4 + a_3^2)x^6 + \cdots \tag{9}$$

When such operations are carried out the region of convergence may be changed. For example, we may write power series for $\sin x$ and for $\cos x$ that converge for all values of x, and yet on division we obtain a power series for $\tan x$ that is convergent only in the region $-\pi/2$ to $\pi/2$.

In exceptional cases, the function cannot be expanded in a power series. The best-known function of this type is $e^{-\frac{1}{x^2}}$, which expanded in the usual way gives a series converging to zero, because each term is zero. Such cases are very seldom encountered in practice.

If the infinite power series is differentiated a number of times, the derivatives obtained are

$$f'(x) = a_1 + 2a_2x + 3a_3x^2 + 4a_4x^3 + 5a_5x^4 + \cdots$$
$$f''(x) = 2a_2 + 6a_3x + 12a_4x^2 + 20a_5x^3 + \cdots$$
$$f'''(x) = 6a_3 + 24a_4x + 60a_5x^2 + \cdots$$

Substituting $x = 0$ in each of these, as well as in the original series (7), there results

$$a_0 = f(0); \qquad a_1 = f'(0); \qquad a_2 = \frac{f''(0)}{2!}; \qquad a_3 = \frac{f'''(0)}{3!}$$
$$a_4 = \frac{f''''(0)}{4!}; \qquad a_n = \frac{f^n(0)}{n!}; \text{ etc.}$$

When these values of the constants are replaced in the original series (7),

$$f(x) = f(0) + f'(0)x + \frac{x^2}{2!}f''(0) + \frac{x^3}{3!}f'''(0) + \cdots \quad (10)$$

This is Maclaurin's series, which may be used to determine a power series to represent a function. It is a special case of Taylor's series, which is

$$f(x) = a_0 + a_1(x - a) + a_2(x - a)^2 + a_3(x - a)^3 + \cdots \quad (11)$$

By the same procedure employed above, the coefficients may be evaluated and the function rewritten as

$$f(x) = f(a) + f'(a)(x - a) + \frac{f''(a)}{2!}(x - a)^2 + \frac{f'''(a)}{3!}(x - a)^3 + \cdots \quad (12)$$

Taylor's series may be used to represent the function for any value of x, provided that the arbitrary constant a is so chosen as to make the series converge.

As an example, expand $\ln (1 + x)$ in Maclaurin's series.

$$a_0 = \ln 1 = 0$$

$$a_1 = f'(0) = \frac{d}{dx}[\ln (1 + x)] = 1$$

$$a_2 = f''(0) = \frac{d}{dx}\left(\frac{1}{1 + x}\right) = -1$$

$$a_3 = f'''(0) = \frac{d}{dx}\left(\frac{-1}{(1 + x)^2}\right) = 2; \text{ etc.}$$

whence

$$\ln (1 + x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \cdots \quad (13)$$

This converges only when $-1 < x < 1$ or for values of $1 + x$ between 0 and 2.

Referring to (13), it will be noted that the series converges very rapidly if x is a small fraction, *i.e.*, the terms soon become negligible. If x is less than 0.05, all terms but the first may be neglected without introducing an error of more than 3 per cent, and $\ln (1 + x)$ may be taken equal to x. Thus ln 1.05 is 0.04879. This is a useful approximation to remember.

Taylor's series is useful in extending the region of definition of a function known only in the form of a power series. If a

represents any value of x within the interval of convergence of the original series (7), the series (12) may be formed by computing all the derivatives at $x = a$. Not infrequently, the interval of convergence of this new series extends beyond that of the original series. By selecting a new value of a within the interval of convergence of the new series, the derivatives at the new value of a may be computed and their substitution into (12) gives a third series, which may extend the definition of $f(x)$ over a still wider range.

Taylor's series for two or more independent variables may be obtained as expansions of $f(x,y)$ $f(x,y,z)$, etc. The derivation need not be given here, but the result has considerable utility. The expansion of a function $f(x,y)$ about a point (a,b) is given by

$$f(x,y) = f(a,b) + \left[(x-a)\frac{\partial f}{\partial x} + (y-b)\frac{\partial f}{\partial y} \right] + \frac{1}{2!}\left[(x-a)^2\frac{\partial^2 f}{\partial x^2} + 2(x-a)(y-b)\frac{\partial^2 f}{\partial x\,\partial y} + (y-b)^2\frac{\partial^2 f}{\partial y^2} \right] + \cdots + \frac{1}{n!}\left[(x-a)\frac{\partial}{\partial x} + (y-b)\frac{\partial}{\partial y} \right]^n f + \cdots \quad (14)$$

where each derivative is to be taken at the point a, b. The meaning of the general term will be evident by comparison with the third term, which is for $n = 2$.

As a simple example, consider the expansion of ye^x about the point $x = a$, $y = b$. The derivatives needed for the series through the third-degree terms are

$$\frac{\partial f}{\partial x} = ye^x = be^a; \qquad \frac{\partial f}{\partial y} = e^x = e^a; \qquad \frac{\partial^2 f}{\partial x^2} = ye^x = be^a;$$
$$\frac{\partial^2 f}{\partial x\,\partial y} = e^x = e^a; \qquad \frac{\partial^2 f}{\partial y^2} = 0; \qquad \frac{\partial^3 f}{\partial x^3} = ye^x = be^a;$$
$$\frac{\partial^3 f}{\partial x^2\,\partial y} = e^x = e^a; \qquad \frac{\partial^3 f}{\partial x\,\partial y^2} = 0; \qquad \frac{\partial^3 f}{\partial y^3} = 0.$$

Hence the series is

$$f(x,y) = be^a + (x-a)be^a + (y-b)e^a + \tfrac{1}{2}(x-a)^2be^a + (x-a)(y-b)e^a + \tfrac{1}{6}(x-a)^3be^a + \tfrac{1}{3}(x-a)^2(y-b)e^a + \cdots \quad (15)$$

The procedure outlined provides a method for evaluating the coefficients in the series

$$f(x,y) = a_0 + a_1x + a_2y + a_3x^2 + a_4xy + a_5y^2 + a_6x^3 + a_7x^2y + a_8xy^2 + a_9y^3 + a_{10}x^4 + \cdots \quad (16)$$

In general, any continuous function may be expressed in a power series of this type in the region in which it has derivatives.

90. Use of Series in the Solution of Ordinary Differential Equations. *a. Taylor's Series.* If a differential equation may be expressed as

$$\frac{dy}{dx} = f(x,y)$$

we may obtain the second and higher derivatives directly and express y by means of a Taylor's series. For example, in the simple case

$$\frac{dy}{dx} = f(x,y) = x + y^2 \quad (17)$$

where $y = b$ at $x = a$, we have from Eq. (25) of Par. 74

$$\frac{d^2y}{dx^2} = \frac{\partial f}{\partial x} + \frac{\partial f}{\partial y}\frac{dy}{dx} = 1 + 2y\frac{dy}{dx}; \qquad \left(\frac{d^2y}{dx^2}\right)_a = 1 + 2ab + 2b^3$$

$$\frac{d^3y}{dx^3} = \frac{\partial^2 f}{\partial x^2} + 2\frac{\partial^2 f}{\partial x\,\partial y}\frac{dy}{dx} + \frac{\partial^2 f}{\partial y^2}\left(\frac{dy}{dx}\right)^2 + \frac{\partial f}{\partial y}\frac{d^2y}{dx^2} = 2\left(\frac{dy}{dx}\right)^2 + 2y\frac{d^2y}{dx^2};$$

$$\left(\frac{d^3y}{dx^3}\right)_a = 2(a^2 + 4ab^2 + b + 3b^4); \text{ etc.}$$

If these values are substituted in the Taylor's series (12),

$$y = b + (a + b^2)(x - a) + \frac{1}{2!}(1 + 2ab + 2b^3)(x - a)^2 + \frac{2}{3!}(a^2 + 4ab^2 + b + 3b^4)(x - a)^3 + \cdots \quad (18)$$

If we assume the curve to pass through the point $y = 0$ at $x = 1$, *i.e.*, $b = 0$, $a = 1$, then the solution is

$$y = (x - 1) + \frac{(x - 1)^2}{2} + \frac{(x - 1)^3}{3} + \frac{(x - 1)^4}{4} + \frac{11}{60}(x - 1)^5 + \cdots \quad (19)$$

b. Power Series. An alternative and usually more direct procedure is to assume that the integral may be expanded in a power series, which is then substituted in the differential equa-

tion. The coefficients, with the exception of the necessary number of arbitrary constants, are obtained by equating coefficients of terms of like powers. This method, like the preceding one, is restricted to cases where it is possible to express the function by means of a power series. The utility of both methods is limited in practice to the solution of linear equations.

Following the same example discussed above in connection with the use of Taylor's series, we first assume that y may be expanded in a power series.

$$y = a_0 + a_1x + a_2x^2 + a_3x^3 + \cdots \tag{20}$$

whence

$$y^2 = a_0^2 + 2a_0a_1x + (2a_0a_2 + a_1^2)x^2 + (2a_0a_3 + 2a_1a_2)x^3 + \cdots$$

and

$$\frac{dy}{dx} = a_1 + 2a_2x + 3a_3x^2 + 4a_4x^3 + \cdots$$

When these are substituted in the differential Eq. (17),

$$a_1 + 2a_2x + 3a_3x^2 + 4a_4x^3 + \cdots = a_0^2 + (1 + 2a_0a_1)x + (2a_0a_2 + a_1^2)x^2 + (2a_0a_3 + 2a_1a_2)x^3 + \cdots$$

We may equate the coefficients of like powers of x; this process gives

$$a_1 = a_0^2; \qquad a_2 = a_0^3 + \frac{1}{2}; \qquad a_3 = a_0^4 + \frac{a_0}{3}; \qquad a_4 = a_0^5 + \frac{5}{12}a_0^2;$$

$$a_5 = a_0^6 + \frac{1}{2}a_0^3 + \frac{1}{20}; \text{ etc.}$$

The solution is

$$y = a_0 + a_0^2x + \left(a_0^3 + \frac{1}{2}\right)x^2 + \left(a_0^4 + \frac{a_0}{3}\right)x^3 + \left(a_0^5 + \frac{5}{12}a_0^2\right)x^4 + \left(a_0^6 + \frac{1}{2}a_0^3 + \frac{1}{20}\right)x^5 + \cdots \tag{21}$$

If we choose the arbitrary constant a_0 so that the curve goes through the origin, then from (20) $a_0 = 0$, and we have $a_1 = 0$; $a_2 = \frac{1}{2}$; $a_3 = 0$; $a_4 = 0$; $a_5 = \frac{1}{20}$; $a_6 = 0$; $a_7 = 0$; $a_8 = \frac{1}{160}$; etc.; whence

$$y = \tfrac{1}{2}x^2 + \tfrac{1}{20}x^5 + \tfrac{1}{160}x^8 + \cdots \tag{22}$$

If we specify that the function shall pass through $y = 0$ at $x = 1$, as in the preceding problem, then we may shift the

coordinates so that the origin will be at this point, in order to compare the result with (19). The differential equation is now

$$\frac{dy}{dx'} = x' + y^2 + 1 \tag{23}$$

and the procedure is the same as before. Since $y = 0$ at $x' = 0$, a_0 is 0. We obtain $a_1 = 1$; $a_2 = \frac{1}{2}$; $a_3 = \frac{1}{3}$; $a_4 = \frac{1}{4}$; $a_5 = \frac{11}{60}$; etc.; whence

$$y = x' + \frac{(x')^2}{2} + \frac{(x')^3}{3} + \frac{(x')^4}{4} + \frac{11}{60}(x')^5 + \cdots \tag{24}$$

which is identical with the result (19) obtained by Taylor's series when expressed in the original coordinate system.

The difficulty of using the power-series method of solving differential equations naturally depends greatly on the form of the equation. The example chosen involved squaring the series for y, which would not be encountered in the solution of

$$\frac{dy}{dx} = x^2 + y \tag{25}$$

It will be apparent that the procedure described would be very easy in the latter case although simpler methods of solution of this form have been presented in Chap. II. In some cases, a substitution of variables will simplify the operations. For example, in

$$\frac{dy}{dx} = x + y^{\frac{1}{2}} \tag{26}$$

we may replace y by p^2 and get

$$2p\frac{dp}{dx} = x + p$$

so that the problem of taking the square root of a series is replaced by the more familiar process of multiplying one series by another.

The solution of a second-order equation by the use of power series proceeds in the same manner as outlined above. As a simple example, we may take

$$\frac{d^2y}{dx^2} + \frac{dy}{dx} = y \tag{27}$$

Let

$$y = a_0 + a_1x + a_2x^2 + a_3x^3 + \cdots \tag{28}$$

$$\frac{dy}{dx} = a_1 + 2a_2x + 3a_3x^2 + 4a_4x^3 + \cdots \tag{29}$$

$$\frac{d^2y}{dx^2} = 2a_2 + 6a_3x + 12a_4x^2 + 20a_5x^3 + \cdots \tag{30}$$

Substituting in the differential equation, we have

$$a_0 + a_1x + a_2x^2 + a_3x^3 + \cdots = a_1 + 2a_2x + 3a_3x^2 + 4a_4x^3 + \cdots + 2a_2 + 6a_3x + 12a_4x^2 + 20a_5x^3 + \cdots \tag{31}$$

Equating coefficients of like powers of x gives

$$a_2 = \tfrac{1}{2}(a_0 - a_1); \qquad a_3 = \tfrac{1}{6}(2a_1 - a_0);$$
$$a_4 = \tfrac{1}{12}(a_0 - \tfrac{3}{2}a_1); \text{ etc.}$$

It is evident that the coefficients will be expressed in terms of the two arbitrary constants a_0 and a_1. The result may be expressed as the sum of two power series, one involving a_0 and the other a_1, each of which is a particular solution of the equation. Since the equation is of the second order, the series with both constants is the complete integral.

91. Fourier Series. The value of infinite series in the solution of differential equations was pointed out in Par. 87. Functions of special value in connection with differential equations are those which bear some peculiar relation to their derivatives. For example, the derivative of $\sin x$ is $\cos x$, and the second derivative is $-\sin x$, *i.e.*, $f''(x) = -f(x)$. Infinite series having such properties are of equal value in the solution of differential equations and, at the same time, may be employed to represent various types of functions. An infinite series of sines and cosines, called a "Fourier series," is especially valuable in the solution of important differential equations. Other types of infinite series, such as Bessel functions, are of importance for the same reason. The problem of finding a Fourier series to represent a function $f(x)$ will be discussed in the present section, the question of how they are used being left to Chap. VI.

A Fourier series is an infinite series of the form

$$f(x) = \frac{a_0}{2} + a_1 \cos x + a_2 \cos 2x + a_3 \cos 3x + \cdots + b_1 \sin x + b_2 \sin 2x + b_3 \sin 3x + \cdots \tag{32}$$

It may be shown that any function may be represented by such a series in the region $x = -\pi$ to $x = \pi$, if it does not "double back" to give more than one value at a single value of x, and provided that it is finite and continuous. It may have sudden jumps or discontinuities, provided that these are finite.

92. Determination of Constants in Fourier Series. Multiply each term of (32) by dx, and integrate term by term in the interval $-\pi$ to π. It will be found that all terms on the right except the first drop out; this process gives

$$\int_{-\pi}^{\pi} f(x)dx = a_0\pi$$

from which,

$$a_0 = \frac{1}{\pi}\int_{-\pi}^{\pi} f(x)dx \tag{33}$$

To obtain the general coefficient a_n, multiply (32) by $\cos nx\,dx$, and integrate again from $-\pi$ to π.

$$\int_{-\pi}^{\pi} f(x)\cos nx\,dx = \frac{a_0}{2}\int_{-\pi}^{\pi}\cos nx\,dx + a_1\int_{-\pi}^{\pi}\cos x\cos nx\,dx + b_1\int_{-\pi}^{\pi}\sin x\cos nx\,dx + b_2\int_{-\pi}^{\pi}\sin 2x\cos nx\,dx + \cdots$$

It is found that all terms on the right are zero except

$$a_n\int_{-\pi}^{\pi}\cos^2 nx\,dx$$

which is equal to $a_n\pi$, so that

$$a_n = \frac{1}{\pi}\int_{-\pi}^{\pi} f(x)\cos nx\,dx \tag{34}$$

Similarly, to obtain b_n, multiply (32) by $\sin nx\,dx$, and integrate from $-\pi$ to π; this process gives

$$b_n = \frac{1}{\pi}\int_{-\pi}^{\pi} f(x)\sin nx\,dx \tag{35}$$

The general coefficient having been evaluated, it is necessary to use only (33), (34), and (35) to build up a series of the type (32) for any function.

As an example, suppose it is desired to expand the function

$$f(x) = 1 - x \tag{36}$$

in a Fourier series in the interval $-\pi$ to π. Substituting in (33), and (34), and (35) yields

$$a_0 = \frac{1}{\pi}\int_{-\pi}^{\pi}(1 - x)dx = 2$$

$$a_n = \frac{1}{\pi}\int_{-\pi}^{\pi}(1 - x)\cos nx\,dx = 0$$

$$b_n = \frac{1}{\pi}\int_{-\pi}^{\pi}(1 - x)\sin nx\,dx = \frac{2}{n}(-1)^n$$

Actually, the integral gives $b_n = -(2/n)$ if n is an odd integer and $b_n = 2/n$ if n is even. This is taken into account in the preceding way of expressing b_n. The resulting series is

$$1 - x = 1 - 2\sin x + \sin 2x - \tfrac{2}{3}\sin 3x + \tfrac{1}{2}\sin 4x + \cdots \quad (37)$$

The result is really 1 minus a sine series for x, and it is apparent that

$$x = 2[\sin x - \tfrac{1}{2}\sin 2x + \tfrac{1}{3}\sin 3x - \tfrac{1}{4}\sin 4x + \cdots] \quad (38)$$

Whether or not the series obtained is one of sines or cosines only or is made up of both sines and cosines depends on whether

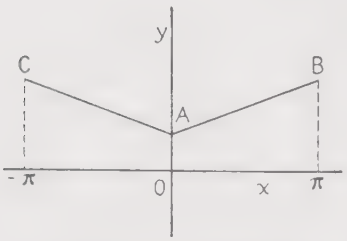

FIG. 46.—Even function.

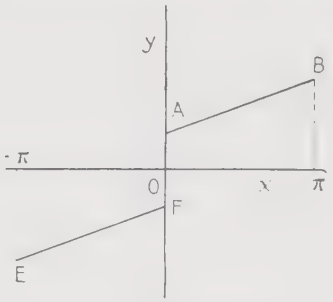

FIG. 47.—Odd function.

the function is even or odd, or neither. An even function, illustrated by Fig. 46, is one in which $f(x) = f(-x)$. The two branches on either side of the y axis are mirror images. An odd function is one in which $f(x) = -f(-x)$, as illustrated by Fig. 47. If the function is even,

$$a_n = \frac{1}{\pi}\int_{-\pi}^{\pi} f(x)\cos nx\,dx = \frac{2}{\pi}\int_{0}^{\pi} f(x)\cos nx\,dx \quad (39)$$

and

$$b_n = \frac{1}{\pi}\int_{-\pi}^{\pi} f(x)\sin nx\,dx = 0 \quad (40)$$

The last result follows because $f(x)$ is the same at $-x$ and x, whereas $\sin nx$ has the opposite sign at $-x$ as at x. The integral from $-\pi$ to 0 is therefore equal to but of opposite sign from the integral from 0 to π.

If the function is odd,

$$a_n = \frac{1}{\pi}\int_{-\pi}^{\pi} f(x) \cos nx \, dx = 0 \tag{41}$$

and

$$b_n = \frac{2}{\pi}\int_{0}^{\pi} f(x) \sin nx \, dx \tag{42}$$

It is obvious that the sine terms disappear in the expansion of even functions and the cosine terms disappear in the expansion of odd functions. Thus, even functions are expanded in cosine series, and odd functions in sine series.

This result suggests a means of choosing either a sine or cosine series for the expression of a function such as AB of Fig. 46, provided that it is permissible to limit the variation of x to the region 0 to π. If a cosine series is desired, the function represented by CA is defined for the interval $-\pi$ to 0 such that $f(-x) = f(x)$ and a_n is evaluated by (39) where the integration is carried out using the function CAB. If a sine series is desired, the function indicated by EF of Fig. 47 is defined so that

$$f(-x) = -f(x),$$

and b_n is evaluated by (42).

As an example, suppose it is desired to express the function $f(x) = 1$ by a sine series in the region 0 to π. The function $f(-x) = -1$ is defined to complete the odd function in the whole interval $-\pi$ to π, and b_n is obtained from (42) as

$$b_n = \frac{2}{\pi}\int_{0}^{\pi} \sin nx \, dx$$

This is $4/n\pi$ when n is odd and zero when n is even. It may be written

$$b_n = \frac{2}{n\pi}[1 - (-1)^n]$$

From (33),

$$a_0 = \frac{1}{\pi}\int_{-\pi}^{\pi} f(x)dx = \frac{1}{\pi}\int_{0}^{\pi} dx + \frac{1}{\pi}\int_{-\pi}^{0} (-dx) = 0$$

The case is chosen so that a_n will be zero. Substituting in (32) gives

$$1 = \frac{4}{\pi}\left[\sin x + \frac{1}{3}\sin 3x + \frac{1}{5}\sin 5x + \cdots\right] \tag{43}$$

Figure 48 indicates the way in which the function is built up by the series. The series plotted is the sine series enclosed by the square brackets of (43). If an infinite number of terms are

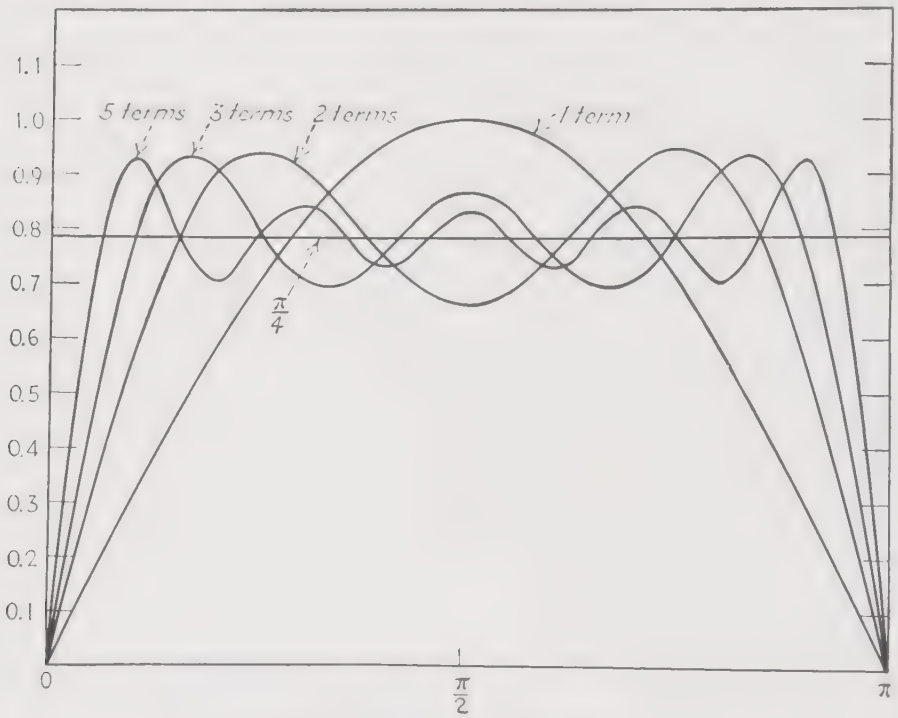

FIG. 48.—Summation of sine terms.

added, the result is π 4, or 0.7854, represented by the solid horizontal line. The single sine term represents the function poorly, and even five terms do not show good agreement. It is apparent that the series converges slowly in the region 0 to π.

If Fourier series are to be used generally, it is necessary to be able to remove the restriction that they should apply only in the interval $-\pi$ to π. This is easily done by replacing x by $p = \pi x / C$, where C is any constant. The function $f_1(x)$ to be expanded in a Fourier series may be written

$$f_1(x) = f_1\left(\frac{pC}{\pi}\right) = f_2(p) \tag{44}$$

The function $f_2(p)$ is then expanded in the regular way by the use of the following equations

$$a_0 = \frac{1}{\pi}\int_{-\pi}^{\pi} f_2(p)dp = \frac{1}{C}\int_{-C}^{C} f_1(x)dx \tag{45}$$

$$a_n = \frac{1}{\pi}\int_{-\pi}^{\pi} f_2(p)\cos np\,dp = \frac{1}{C}\int_{-C}^{C} f_1(x)\cos\frac{n\pi x}{C}dx \tag{46}$$

$$b_n = \frac{1}{\pi}\int_{-\pi}^{\pi} f_2(p)\sin np\,dp = \frac{1}{C}\int_{-C}^{C} f_1(x)\sin\frac{n\pi x}{C}dx \tag{47}$$

The variable p is replaced by $\pi x\ C$ in the series obtained, which is then an expansion of $f_1(x)$ in the interval $-C$ to C.

As an example of this change of variables, obtain a Fourier series to represent the function $f(x) = 2$ in the interval -2 to 0, $f(x) = x$ in the interval 0 to 2. Figure 49 indicates the nature of this function, having a discontinuity at $x = 0$.

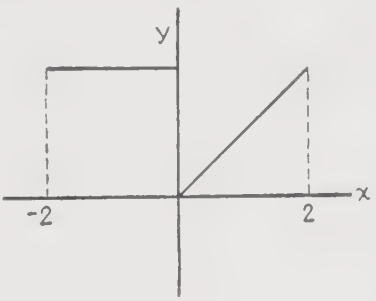

FIG. 49.

Following the procedure outlined above, let $x = 2p/\pi$, whence

$$f_1(x) = f_2(p) = \frac{a_0}{2} + a_1\cos p + a_2\cos 2p + a_3\cos 3p + b_1\sin p + b_2\sin 2p + b_3\sin 3p + \cdots$$

From (45), (46), and (47),

$$a_0 = \frac{1}{\pi}\int_{-\pi}^{\pi} f_2(p)dp = \frac{1}{2}\int_{-2}^{2} f_1(x)dx = \frac{1}{2}\int_{-2}^{0} 2dx + \frac{1}{2}\int_{0}^{2} x\,dx = 3$$

$$a_n = \frac{1}{2}\int_{-2}^{2} f_1(x)\cos\frac{n\pi x}{2}dx = \frac{1}{2}\int_{-2}^{0} 2\cos\frac{n\pi x}{2}dx + \frac{1}{2}\int_{0}^{2} x\cos\frac{n\pi x}{2}dx$$

$$= -\frac{4}{n^2\pi^2}$$

when n is odd, and zero when n is even.

$$b_n = \frac{1}{C}\int_{-C}^{C} f_1(x)\sin\frac{n\pi x}{C}dx = \frac{1}{2}\int_{-2}^{0} 2\sin\frac{n\pi x}{2}dx + \frac{1}{2}\int_{0}^{2} x\sin\frac{n\pi x}{2}dx$$

$$= -\frac{2}{n\pi}$$

The coefficients being substituted, the series is obtained as

$$f(x) = \frac{3}{2} - \frac{4}{\pi^2}\left(\cos\frac{\pi x}{2} + \frac{1}{9}\cos\frac{3\pi x}{2} + \frac{1}{25}\cos\frac{5\pi x}{2} + \cdots\right) - \frac{2}{\pi}\left(\sin\frac{\pi x}{2} + \frac{1}{2}\sin\frac{2\pi x}{2} + \frac{1}{3}\sin\frac{3\pi x}{2} + \cdots\right) \quad (48)$$

At $x = 0$, where the discontinuity occurs, the series reduces to

$$f(0) = \frac{3}{2} - \frac{4}{\pi^2}\left(1 + \frac{1}{9} + \frac{1}{25} + \cdots\right)$$

The last series may be shown to equal $\pi^2/8$, whence $f(0) = 1$. Thus the series gives a value just half-way between the two limits of 2 and 0 at $x = 0$. It is true, in general, that the Fourier series will give the arithmetic mean of the two values of the function at a discontinuity.

93. Bessel Functions. Consider the following problem: A copper fin 1 ft. long is triangular in cross section, being 1 in.

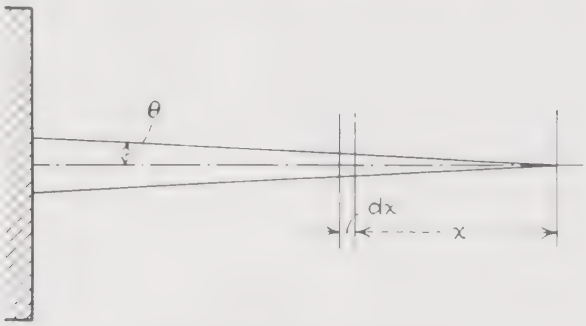

FIG. 50.—Wedge-shaped fin.

wide at the base and tapering off to a point. The base of this wedge-shaped piece of metal is maintained at a constant temperature of 200°F., and the fin loses heat by convection to the surrounding air at 100°F. The surface coefficient of heat transfer is 2.0 B.t.u. (ft.) (hr.)(sq. ft.)(°F.). What is the relation between the temperature of the fin metal and the distance from the base?

The fin is shown diagrammatically in Fig. 50. Let t represent the temperature at a distance x ft. from the tip, and for simplicity assume that the temperature variation through the fin in a direction parallel to the base may be neglected. Let t_B represent the temperature of the base and t_a the temperature of the air. Take a basis of 1 ft. of fin in a direction parallel to the base, so that the cross section of the fin at any distance x from the tip is $x/12$ sq. ft.

In order to set up the differential equation, make a heat balance on the fin element dx. The rate of heat input by conduction across a plane at x (q is taken as positive when heat flows in the direction of increasing x) is

$$q = -k\frac{x}{12}\frac{dt}{dx} \text{ B.t.u. per hr.}$$

At $x + dx$, the rate of heat output by conduction is

$$q + dq = -k\left(\frac{x + dx}{12}\right)\left[\frac{dt}{dx} + d\left(\frac{dt}{dx}\right)\right] \tag{49}$$

and the net rate of heat input to the element by conduction is

$$-dq = \frac{k}{12}\left[\frac{dt}{dx}dx + xd\left(\frac{dt}{dx}\right)\right] \tag{50}$$

The perimeter of the wedge 1 ft. wide is 2 ft., and the rate of heat loss from the surface is

$$dq_s = h(t - t_a)2 \sec\theta\, dx \tag{51}$$

The wedge is so flat that sec θ may be taken as unity. The heat balance, net input $-$ output $= 0$, is written

$$h(t - t_a)2dx = \frac{k}{12}\left[\frac{dt}{dx}dx + xd\left(\frac{dt}{dx}\right)\right] \tag{52}$$

Substituting $h = 2$ and dividing by dx result in

$$\frac{48}{k}(t - t_a) = \frac{dt}{dx} + x\frac{d^2t}{dx^2}$$

or

$$x\frac{d^2t}{dx^2} + \frac{dt}{dx} - \beta(t - t_a) = 0 \tag{53}$$

where $\beta = 48\ k = 48\ 220 = 0.218$. If we let y replace $(t - t_a)$ then the equation reduces to

$$x\frac{d^2y}{dx^2} + \frac{dy}{dx} - \beta y = 0 \tag{54}$$

This equation may be solved by the use of a power series as described in Par. 90. Assume that y may be represented by an infinite power series

$$y = a_0 + a_1x + a_2x^2 + a_3x^3 + \cdots$$
$$\frac{dy}{dx} = a_1 + 2a_2x + 3a_3x^2 + 4a_4x^3 + \cdots$$
$$x\frac{d^2y}{dx^2} = 2a_2x + 6a_3x^2 + 12a_4x^3 + 20a_5x^4 + \cdots$$

Substituting this series in Eq. (54) gives

$$\beta a_0 - a_1 + (\beta a_1 - 4a_2)x + (\beta a_2 - 9a_3)x^2 + (\beta a_3 - 16a_4)\,x^3 + \cdots = 0$$

Equating coefficients of like terms results in

$$a_1 = \beta a_0; \qquad a_2 = \frac{\beta a_1}{4} = \frac{\beta^2 a_0}{4}; \qquad a_3 = \frac{\beta^3 a_0}{36}$$

and

$$a_n = \frac{\beta^n a_0}{n^2(n-1)^2(n-2)^2 \cdots 4 \times 1}$$

Hence the result is

$$y = t - 100 = a_0\left(1 + \beta x + \frac{\beta^2 x^2}{4} + \frac{\beta^3 x^3}{36} + \frac{\beta^4 x^4}{576} + \cdots\right) \tag{55}$$

When $\beta = 0.218$ and the value $t = 200$ are substituted at $x = 1$, a_0 is evaluated as 81.2°, which means that the temperature of the tip of the fin ($x = 0$) is 181.2°F. The complete numerical solution is, therefore

$$t - 100 = 81.2(1 + 0.218 + 0.0118x^2 + 0.0028x^3 + \cdots)$$

In connection with this problem, two details are worthy of note. x is defined as the distance from the tip rather than from the base, and care is taken to equate *minus* dq to $h(t - t_a)dA$. The first merely permits a simplification of the algebra. The omission of the negative sign at the point noted would have led to a ridiculous result.

The illustrative example just discussed is intended to bring out the relative simplicity of the solution of a Bessel equation by means of a Bessel function.

The differential equation (54) is a typical Bessel equation, and the result (55) is a Bessel function. Bessel functions are of importance because they are defined as "solutions of the Bessel equation," which is a differential equation encountered in many practical problems.

The simplest Bessel function is

$$J_0(x) = 1 - \frac{x^2}{2^2} + \frac{x^4}{2^2 4^2} - \frac{x^6}{2^2 4^2 6^2} + \cdots \tag{56}$$

The symbol $J_0(x)$ is simply an abbreviation for the series and is called a "Bessel function of the zero order." If this series is differentiated with respect to x and the derivative multiplied by x, the result is

$$x\frac{dJ_0(x)}{dx} = -\frac{x^2}{2} + \frac{x^4}{2^2 4} - \frac{x^6}{2^2 4^2 6} + \cdots \tag{57}$$

If (56) is differentiated twice and multiplied by x^2, the result is

$$x^2\frac{d^2J_0(x)}{dx^2} = -\frac{x^2}{2} + \frac{3x^4}{2^2 4} - \frac{5x^6}{2^2 4^2 6} \cdots \tag{58}$$

When these results are combined, it is found that

$$x^2\frac{d^2J_0(x)}{dx^2} + x\frac{dJ_0(x)}{dx} + x^2J_0(x) = 0$$

From this, it is evident that $y = J_0(x)$ is a solution of the equation

$$x^2\frac{d^2y}{dx^2} + x\frac{dy}{dx} + x^2y = 0 \tag{59}$$

Various mathematical tables* give values of the series (56) for different values of x, and the solution of practical problems is simplified by having the numerical values of $J_0(x)$ available.

A more general form of the Bessel equation is

$$x^2\frac{d^2y}{dx^2} + x\frac{dy}{dx} + (x^2 - n^2)y = 0 \tag{60}$$

This may be solved by power series, as was done above, but the difficulty encountered depends considerably on the numerical value of the constant n. Because the equation is of the second order, the general solution must involve two arbitrary constants and is usually written as the sum of two functions, each intro-

* BYERLY, "Fourier Series and Spherical Harmonics," Ginn and Company, Boston, 1893; JAHNKE-EMDE, "Funktiontafeln," B. G. Teubner, Leipzig, 1933; GRAY, MATHEWS, and MACROBERT, "Bessel Functions," Macmillan & Company, Ltd., London, 1931; "British Association Mathematical Tables," Vol. VI, Cambridge University Press, 1937. The last is the most complete and probably the most accurate.

ducing, or being multiplied by, an arbitrary constant (Par. 50). The functions so employed are Bessel functions, since they are necessarily solutions of the Bessel equation. The two functions employed must be independent solutions of the equation if the two desired constants are to be introduced. A variety of types of such functions have been discovered and the relations between them developed. The series $J_0(x)$ is a special case of the type most frequently used, the general series being written $J_n(x)$. When n is zero or a positive integer, $J_n(x)$ is defined by the series

$$J_n(x) = \frac{x^n}{2^n \cdot n!}\left[1 - \frac{x^2}{2(2n+2)} + \frac{x^4}{2\cdot 4(2n+2)(2n+4)} - \frac{x^6}{2\cdot 4\cdot 6(2n+2)(2n+4)(2n+6)} + \cdots\right]$$

$$= \sum_{k=0}^{k=\infty} (-1)^k \frac{x^{n+2k}}{2^{n+2k} k!(n+k)!} \tag{61}$$

Noting that 0! is taken as unity, we can easily see that this reduces to (56) for $n = 0$. If n is a negative integer, we have the relation

$$J_{-n}(x) = (-1)^n J_n(x) \tag{62}$$

which need not be proved here. A solution of (60) in the form

$$y = AJ_n(x) + BJ_{-n}(x) \tag{63}$$

consequently reduces to

$$y = [A + (-1)^n B]J_n(x) \tag{64}$$

which has only one arbitrary constant and consequently cannot be a general solution of (60).

If n is a fraction, we have

$$J_n(x) = \sum_{k=0}^{k=\infty} \frac{(-1)^k x^{n+2k}}{2^{n+2k} k!\Gamma(n+k+1)} \tag{65}$$

where $\Gamma(n+k+1)$ represents the "gamma function" of $n+k+1$. The gamma function is defined by the definite integral

$$\Gamma(n) = \int_0^\infty x^{n-1} e^{-x} dx \qquad (n > 0)$$

When n is a positive integer, it may be shown that

$$\Gamma(n+1) = n\Gamma(n) = n!$$

and this may be taken as a generalization of $n!$ for fractional and negative values of n. When this relation is used, (65) follows from (61). Numerical values of gamma functions are tabulated in many mathematical tables.* When n is a fraction, (62) does not hold; and both $J_n(x)$ and $J_{-n}(x)$ are independent solutions of (60), and (63) is a general solution of (60) for fractional values of n.

Another function that satisfies (60) is defined by the series†

$$Y_n(x) = \frac{2}{\pi}\left(\gamma + \ln\frac{x}{2}\right)J_n(x) - \frac{1}{\pi}\sum_{r=0}^{r=n-1}\frac{(n-r-1)!\,x^{-n+2r}}{2^{-n+2r}r!} - \frac{1}{\pi}\sum_{k=0}^{k=\infty}\frac{(-1)^k x^{n+2k}}{2^{n+2k}k!(n+k)!}\left(1+\frac{1}{2}+\frac{1}{3}+\cdots\frac{1}{k}+1+\frac{1}{2}+\frac{1}{3}+\cdots\frac{1}{n+k}\right) \quad (66)$$

where γ is 0.5772157. When n is zero or an integer, this represents an independent solution, and the general solution of (60) is

$$y = AJ_n(x) + BY_n(x) \quad (67)$$

where A and B are arbitrary constants.

The problem of the wedge-shaped fin led to the differential equation (54), which is an example of the more general type

$$x^2\frac{d^2y}{dx^2} + x\frac{dy}{dx} - (x^2+n^2)y = 0 \quad (68)$$

This is the same as (60) if the variable is taken as ix ($i = \sqrt{-1}$). In the solution of this form, it is usually convenient to employ two other Bessel functions

* PEIRCE, B. O., "A Short Table of Integrals," Ginn and Company, Boston, 1929.

† Considerable confusion exists in the standard reference works and tables with regard to the nomenclature used in representing various Bessel functions. We follow the notation employed by the "British Association Mathematical Tables," Vol. VI, "Bessel Functions," in which a section is devoted to relating the various systems of notation.

$$I_n(x) = i^{-n}J_n(ix) \tag{69}$$

where

$$I_n(x) = \sum_{k=0}^{k=\infty} \frac{x^{n+2k}}{2^{n+2k}k!\,\Gamma(n+k+1)} \tag{70}$$

and

$$K_n(x) = (-1)^{n+1}I_n(x)\left(\gamma + \ln\frac{x}{2}\right) + \frac{1}{2}\sum_{s=0}^{s=n-1}\frac{(-1)^s(n-s-1)!}{s!}\left(\frac{x}{2}\right)^{-n+2s} + (-1)^n\frac{1}{2}\sum_{k=0}^{k=\infty}\frac{1}{k!(n+k)!}\left(\frac{x}{2}\right)^{n+2k}\left(1+\frac{1}{2}+\frac{1}{3}+\cdots \frac{1}{k}+1+\frac{1}{2}+\frac{1}{3}+\cdots\frac{1}{n+k}\right) \tag{71}$$

If n is not an integer, $I_n(x)$ and $I_{-n}(x)$ are independent solutions, and the general solution is

$$y = AI_n(x) + BI_{-n}(x) \tag{72}$$

If n is an integer, $I_n(x)$ is again a solution, but $K_n(x)$ is a more convenient independent solution than the $Y_n(ix)$ indicated by (67). Hence we write

$$y = AI_n(x) + BK_n(x) \tag{73}$$

Summarizing, therefore, (63) *is a solution of* (60) *if n is a fraction, whereas the solution* (67) *is used if n is zero or an integer. The solution of* (68) *is best represented by* (72) *if n is a fraction and by* (73) *if n is zero or an integer.*

The importance of the Bessel functions defined lies primarily in their connection with the Bessel equation. The following relations may be easily proved and are valuable in testing a solution to make sure it is correct:

$$\frac{d}{dx}[x^nJ_n(x)] = x^nJ_{n-1}(x) \tag{74}$$

$$\frac{d}{dx}[x^{-n}J_n(x)] = -x^{-n}J_{n+1}(x) \tag{75}$$

$$\frac{dJ_n(x)}{dx} = \frac{n}{x}J_n(x) - J_{n+1}(x) \tag{76}$$

$$J_{n-1}(x) - J_{n+1}(x) = 2\frac{dJ_n(x)}{dx} \tag{77}$$

$$\frac{2n}{x}J_n(x) = J_{n-1}(x) + J_{n+1}(x) \tag{78}$$

From (74) and (62), it follows that if n is zero

$$\frac{d}{dx}J_0(x) = J_{-1}(x) = -J_1(x) \tag{79}$$

The relations (74) to (78), inclusive, hold also for the Y function. The corresponding relations for the I function are

$$\frac{d}{dx}[x^n I_n(x)] = x^n I_{n-1}(x) \tag{80}$$

$$\frac{d}{dx}[x^{-n} I_n(x)] = x^{-n} I_{n+1}(x) \tag{81}$$

$$\frac{d}{dx}[I_n(x)] = \frac{n}{x}I_n(x) + I_{n+1}(x) \tag{82}$$

$$I_{n-1}(x) + I_{n+1}(x) = 2\frac{d}{dx}[I_n(x)] \tag{83}$$

$$\frac{2n}{x}I_n(x) = I_{n-1}(x) - I_{n+1}(x) \tag{84}$$

and when n is an integer

$$I_n(x) = I_{-n}(x) \tag{85}$$

The corresponding relations for the K functions are

$$\frac{d}{dx}[x^n K_n(x)] = -x^n K_{n-1}(x) \tag{86}$$

$$\frac{d}{dx}[x^{-n} K_n(x)] = -x^{-n} K_{n+1}(x) \tag{87}$$

$$\frac{d}{dx}[K_n(x)] = \frac{n}{x}K_n(x) - K_{n+1}(x) \tag{88}$$

$$K_{n-1}(x) + K_{n+1}(x) = -2\frac{d}{dx}[K_n(x)] \tag{89}$$

$$\frac{2n}{x}K_n(x) = K_{n+1}(x) - K_{n-1}(x) \tag{90}$$

$$K_{-n}(x) = K_n(x) \ (n \text{ an integer}) \tag{91}$$

Returning to the problem of the wedge-shaped fin, let us consider how the solution would have been obtained had we

proceeded directly to the use of Bessel functions. The first step is to compare the differential equation with the forms (60) and (68) to evaluate n and the variable x. Multiplying (54) by x gives

$$x^2\frac{d^2y}{dx^2} + x\frac{dy}{dx} - \beta xy = 0$$

In order to avoid confusion with the symbols of (60) and (68), it is rewritten

$$z^2\frac{d^2y}{dz^2} + z\frac{dy}{dz} - \beta zy = 0 \tag{92}$$

By trial, it is found that, if n is taken as zero and x is set equal to $2\sqrt{\beta z}$, (68) becomes identical with (92). This follows from the substitutions

$$\frac{dy}{dx} = \frac{dy}{d(2\sqrt{\beta z})} = \sqrt{\frac{z}{\beta}}\frac{dy}{dz}$$

and

$$\frac{d^2y}{dx^2} = \frac{d}{d(2\sqrt{\beta z})}\left[\sqrt{\frac{z}{\beta}}\frac{dy}{dz}\right] = \frac{z}{\beta}\frac{d^2y}{dz^2} + \frac{1}{2\beta}\frac{dy}{dz}$$

The general solution of (68), for $n = 0$, is given by (73) as

$$y = C_1I_0(x) + C_2K_0(x)$$

whence the solution of (92) is obtained as

$$y = C_1I_0(2\sqrt{\beta z}) + C_2K_0(2\sqrt{\beta z}) \tag{93}$$

It will be remembered that z replaced x in the original solution and represents the distance from the tip of the fin. Since $K_0(2\sqrt{\beta z})$ approaches ∞ as z approaches zero and $I_0(0) = 1$, C_2 must be zero.

$$y = t - 100 = C_1I_0(2\sqrt{\beta z}) = C_1I_0(2\sqrt{0.218z})$$

Since $t = 200$ at $z = 1$, then

$$200 - 100 = C_1I_0(2\sqrt{0.218}) = 1.230C_1$$

the value of 1.230 for $I_0(2\sqrt{0.218})$ being obtained from tables of the function. This makes $C_1 = 81.2$ and gives the final result

$$t - 100 = 81.2I_0(0.934\sqrt{z}) \tag{94}$$

The following values of the temperature along the fin are obtained by a simple calculation from tabulated values of $I_0(z)$:

TABLE XV

z	$0.934\sqrt{z}$	$I_0(0.934\sqrt{z})$	t(°F.)
0	0	1.0	181.2
0.2	0.417	1.0434	184.8
0.4	0.59	1.089	188.5
0.5	0.66	1.112	190.4
0.6	0.722	1.134	192.2
0.8	0.832	1.180	195.9
1.0	0.934	1.230	200.0

As another example of the use of Bessel functions, consider the problem of heat loss from the surface of an oven wall due to "through metal," which conducts heat from the inside, the heat being dissipated to the air from the sheet-metal protective covering of the insulated housing. The metal covering is of steel 0.005 ft. thick, having a thermal conductivity of 25 B.t.u. (hr.)(sq. ft.)(°F./ft.). The surface coefficient of heat loss is 2.5 B.t.u./(hr.)(sq. ft.)(°F.), and the head of the bolt is $\frac{5}{8}$ in. in diameter. The room air is at 70°F., and the temperature of the head of the bolt is constant at 150°F. Neglecting heat loss except by conduction along the bolt, determine the temperature of the outer metal wall at several points up to 1 ft. from the bolt.

In setting up the necessary differential equation, it is important to choose the proper variables. On first thought, it would appear that three variables are involved; temperature, and two variables to define position. Since the temperature function is symmetrical about the bolt head, the single variable r, representing the radial distance from the bolt center, may be used to define position. When the differential heat balance on an annular surface element is set up, the rate of heat input q at radius r is given by

$$q = -ka2\pi r\frac{dt}{dr}$$

At $r + dr$, the rate of heat output is

$$q + dq = -ka2\pi(r + dr)\left[\frac{dt}{dr} + d\left(\frac{dt}{dr}\right)\right]$$

$$= -ka2\pi\left[r\frac{dt}{dr} + rd\left(\frac{dt}{dr}\right) + dt\right]$$

where a represents the thickness of the metal.

The difference $-dq$ is the heat lost to the room, whence

$$-dq = h(t - t_a)2\pi r\,dr = ka2\pi\left[r d\left(\frac{dt}{dr}\right) + dt\right] \tag{95}$$

$$2\pi hr(t - t_a) = ka2\pi\left[r\frac{d^2t}{dr^2} + \frac{dt}{dr}\right]$$

$$\frac{(t_a - t)h}{ka} + \frac{1}{r}\frac{dt}{dr} + \frac{d^2t}{dr^2} = 0 \tag{96}$$

Let $y = t - t_a$, and $\beta = h/ka$; then

$$r^2\frac{d^2y}{dr^2} + r\frac{dy}{dr} - \beta r^2 y = 0 \tag{97}$$

This may be made identical with (68) by letting $x = r\sqrt{\beta}$ and $n = 0$. The solution is again of the same form (48).

$$y = C_1 I_0(r\sqrt{\beta}) + C_2 K_0(r\sqrt{\beta}) \tag{98}$$

This time $I_0(r\sqrt{\beta})$ is eliminated; for it increases with increasing positive values of the variable and could not represent the temperature at large distances from the bolt, which obviously decrease to approach 70°F. as an asymptote. Consequently, the result is

$$t - 70 = C_2 K_0(r\sqrt{\beta}) \tag{99}$$

It is also possible to determine C_1 as zero and hence eliminate $I_0(r\sqrt{\beta})$ by a consideration of the boundary condition $r = \infty$, $y = t - t_a = 0$. At $r = \infty$, we then have

$$C_1 = \frac{-C_2 K_0(r\sqrt{\beta})}{I_0(r\sqrt{\beta})}$$

Since at $r = \infty$, $K_0(r\sqrt{\beta}) = 0$ and $I_0(r\sqrt{\beta}) = \infty$ (see Fig. 51), $C_1 = 0$.

At this point in the solution, it is well to check the validity of the result through the use of Eqs. (86) to (91). From (88),

$$\frac{dy}{dx} = \frac{dK_0(r\sqrt{\beta})}{d(r\sqrt{\beta})} = -K_1(r\sqrt{\beta}) = \frac{1}{\sqrt{\beta}}\frac{dy}{dr} \qquad (r \neq 0)$$

$$\frac{d^2y}{dx^2} = \frac{d[-K_1(r\sqrt{\beta})]}{d(r\sqrt{\beta})} = -\frac{1}{r\sqrt{\beta}}K_1(r\sqrt{\beta}) + K_2(r\sqrt{\beta}) = \frac{1}{\beta}\frac{d^2y}{dr^2}$$

$$(r \neq 0)$$

On substitution in (97), the left-hand side becomes

$$-r\sqrt{\beta}K_1(r\sqrt{\beta}) + r^2\beta K_2(r\sqrt{\beta}) - r\sqrt{\beta}K_1(r\sqrt{\beta}) - r^2\beta K_0(r\sqrt{\beta})$$

From (90) it is seen that the sum of the first and third terms is equal to the sum of the second and fourth terms and the expression reduces to zero. The use of $K_0(r\sqrt{\beta})$ as a solution of (97) is substantiated in this way.

Proceeding with the numerical solution, we have

$$\beta = \frac{h}{ka} = \frac{2.5}{(25 \times 0.005)} = 20,$$

and r_0, the radius of the bolt head, is $5\ (2 \times 8 \times 12) = 0.026$ ft. Hence

$$150 - 70 = C_2K_0(0.026\sqrt{20}) = C_2K_0(0.116) = 2.3C_2$$

from which $C_2 = 34.8$. The final form is

$$t - 70 = 34.8K_0(r\sqrt{20}) \tag{100}$$

The following table gives the temperatures calculated for various values of r:

TABLE XVI

r (ft.)	$r\sqrt{20}$	$K_0(r\sqrt{20})$	t (°F.)
0.05	0.223	1.65	128
0.1	0.446	1.04	106
0.2	0.892	0.493	87
0.4	1.785	0.155	75.5
0.6	2.68	0.051	71.8
0.8	3.57	0.018	70.6
1.0	4.47	0.006	70.2

In the case of an actual oven wall, there is simultaneous conduction through the wall itself. This does not complicate the problem appreciably if it is assumed that such heat conduction is wholly normal to the surface. In setting up the differential equation, the heat balance is obtained by setting dq equal to the sum of the heat "gained" from the room and the heat gained from the inside by the annular element of differential

width. The resulting equation is of the same form and is no more difficult to solve. When the temperature is a function of position on the outer wall face, the heat loss due to the conduction by the bolt may be readily obtained by graphical integration.

In each of the illustrative examples, one of the two terms of the general solution was eliminated because the function was clearly of the wrong type, and one arbitrary constant could be immediately specified as zero. Figure 51 indicates the nature of the zero orders of the several Bessel functions and is an aid in

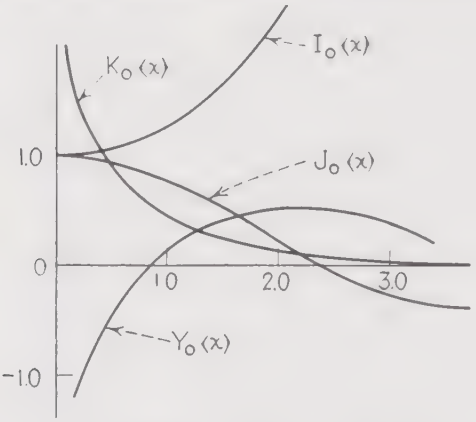

FIG. 51.—Bessel functions of zero order.

visualizing the character of the simpler functions when a simplification of the solution is considered. Similar plots of other orders are given in tables of numerical values of the functions.

94. Solution of Generalized Bessel Equation. Even though the differential equation may be recognized as a Bessel equation, it is not always easy to interpret the solutions outlined above in terms of the variables appearing in the equation. The choice of variable in the Bessel function employed is perhaps the most difficult problem encountered in obtaining the numerical solution. A solution may always be checked by differentiating, but it is clearly desirable to have some general procedure to follow when expressing a solution in terms of the variables appearing in the equation.

An exceedingly valuable tool for this purpose is the general form of the Bessel equation and solution suggested by R. D. Douglass.* The differential equation is written

* Private communication, 1937.

$$x^2\frac{d^2y}{dx^2} + [(1 - 2m)x - 2\alpha x^2]\frac{dy}{dx} + [p^2a^2x^{2p} + \alpha^2x^2 + \alpha(2m - 1)x + m^2 - p^2n^2]y = 0 \quad (101)$$

and the corresponding solution is

$$y = x^m e^{\alpha x}[AJ_n(ax^p) + BY_n(ax^p)] \quad (102)$$

where A and B are arbitrary constants and the other terms are defined by (101).

In the problem of the wedge-shaped fin, the differential equation obtained was

$$z^2\frac{d^2y}{dz^2} + z\frac{dy}{dz} - \beta zy = 0 \quad (92)$$

When this is compared with (101), it is apparent by inspection that $\alpha = 0$; $m = 0$; $p = \frac{1}{2}$; $p^2a^2 = -\beta$; $a = 2i\sqrt{\beta}$; and $n = 0$. We may write the solution immediately from (102).

$$\begin{aligned} y &= AJ_0(2i\sqrt{\beta x}) + BY_0(2i\sqrt{\beta x}) \\ &= AI_0(2\sqrt{\beta x}) + BY_0(2i\sqrt{\beta x}) \end{aligned} \quad (103)$$

This is the same as the solution (93) used above, except that we replaced $Y_0(2i\sqrt{\beta x})$ by the more convenient solution $K_0(2\sqrt{\beta x})$.

In the problem of the bolt in the oven wall, the differential equation (97) was obtained. If this is compared with (101), we find $\alpha = 0$; $m = 0$; $p = 1$; $a^2 = -\beta$; and $n = 0$. Hence, the solution (102) is written

$$\begin{aligned} y &= AJ_0(ir\sqrt{\beta}) + BY_0(ir\sqrt{\beta}) \\ &= AI_0(r\sqrt{\beta}) + BY_0(ir\sqrt{\beta}) \end{aligned} \quad (104)$$

In the numerical solution, $Y_0(ir\sqrt{\beta})$ is again replaced by the more convenient solution $K_0(r\sqrt{\beta})$.

As another example, consider the equation

$$x^2\frac{d^2y}{dx^2} - 2\beta x\frac{dy}{dx} + x\frac{dy}{dx} + \beta^2x^{2\beta}y = 0 \quad (105)$$

By comparison with (101) we have $\alpha = 0$; $m = \beta$; $p = \beta$; $a = 1$; and $n = 1$. The solution (102) is

$$y = x^\beta[AJ_1(x^\beta) + BY_1(x^\beta)]$$

If this general method is employed, it is usually convenient to replace $Y_n(x)$ by $J_{-n}(x)$ and $Y_n(ix)$ by $I_{-n}(x)$ if n is a fraction and $Y_n(ix)$ by $K_n(x)$ if n is zero or an integer.

CHAPTER VI

PARTIAL DIFFERENTIAL EQUATIONS

95. Nature of a Partial Differential Equation. An equation involving partial derivatives is a partial differential equation. The equation

$$\frac{\partial^2 u}{\partial x\, \partial y} = 0 \tag{1}$$

is a partial differential equation. Such equations are of importance in engineering because the significant variables are so frequently functions of more than one independent variable, and the basic differential expressions for the natural laws are, therefore, partial differential equations. The usual problem is to determine a particular relation between u, x, and y, expressed as $u = f(x,y)$, that satisfies the basic differential equation and also satisfies some particular conditions specified by the practical problem at hand.

Integrating (1) with respect to x gives

$$\frac{\partial u}{\partial y} = f_1(y) \tag{2}$$

and integrating (2) with respect to y gives

$$u = \int f_1(y)dy + f_2(x) = f_3(y) + f_2(x) \tag{3}$$

which may be checked by differentiating with respect to x and y separately and comparing with (1). It will be observed that (3) is a solution of (1), no matter what may be the nature of the functions $f_3(y)$ and $f_2(x)$, which are arbitrary functions. Whereas the solution of ordinary differential equations involves the introduction of arbitrary constants, the solution of partial differential equations involves the introduction of arbitrary functions.

As another illustration, consider the equation

$$\frac{\partial^2 u}{\partial x^2} = a^2 u \tag{4}$$

The general solution is

$$u = c_1 e^{ax} + c_2 e^{-ax} \tag{5}$$

where c_1 and c_2 are any functions not depending on x. If x and y are the only independent variables, this becomes

$$u = e^{ax} f_1(y) + e^{-ax} f_2(y) \tag{6}$$
$$\frac{\partial u}{\partial x} = a e^{ax} f_1(y) - a e^{-ax} f_2(y)$$

and

$$\frac{\partial^2 u}{\partial x^2} = a^2 e^{ax} f_1(y) + a^2 e^{-ax} f_2(y) = a^2 u$$

Here again, arbitrary functions have appeared in the solution, just as arbitrary constants appear in the solution of ordinary differential equations. Something of the reason for these arbitrary functions may be understood by visualizing the geometric representation of (3). For simplicity, take the specific case of $f_3(y) = y$ and $f_2(x) = x$, whence $u = x + y$. This particular solution is represented by a plane at 45 deg. to both the u, x plane and the u, y plane. The derivative $\partial u/\partial y$ is the slope of a line on this plane drawn at a constant value of x, *i.e.*, parallel to the u, y plane. Since the surface is a plane, this line will be straight and its slope constant. Its slope will be $\tan 45° = 1$, no matter what the value of x. Hence $\partial(\partial u/\partial y)/\partial x$, or $\partial^2 u/\partial x\, \partial y$, will be zero as called for by (1). Note that there is an infinite number of surfaces of this type, such as

$$u = 2x + 3y.$$

Since the functions are general, there is an infinite number of types. Thus, there is an infinite number of functions, rather than an infinite number of constants, possible as a result of each integration and a double infinite number of functions possible if the equation, like (1), is of the second order.

In any practical problem, there must be information in addition to the differential equation available if a usable solution is to be obtained. The solution (3) is of no practical value without information that will define the functions $f_3(y)$ and $f_2(x)$. Thus, the usual problem is to obtain any solution of the differential equation (such as $u = x + y$ in the example) that satisfies certain other conditions associated with the physical problem. A number of examples of this process will be discussed below.

96. General Solution of Partial Differential Equations. Many types of partial differential equations are best solved by trial. In some cases, there are standard procedures, as, for example, in the case of linear partial differential equations of the first order. These are of the type

$$P\frac{\partial u}{\partial x} + Q\frac{\partial u}{\partial y} = R \tag{7}$$

where P, Q, and R are functions of u, x, and y. The procedure is to solve the ordinary differential equations

$$\frac{dx}{P} = \frac{dy}{Q} = \frac{du}{R} \tag{8}$$

expressing the result in the form $f_1(x,y,u) = c_1$ and $f_2(x,y,u) = c_2$. The solution to the original equation is $f_3(c_1,c_2) = 0$, where f_3 is an arbitrary function.

For example, if the equation is

$$\frac{\partial u}{\partial x} + \frac{\partial u}{\partial y} = 1 \tag{9}$$

we have

$$dx = dy = du$$

the solutions of which are $x - y = c_1$ and $y - u = c_2$. The solution to (9) is, therefore,

$$f_3[(x - y),(y - u)] = 0 \tag{10}$$

As another example, consider the equation

$$xu\frac{\partial u}{\partial x} + yu\frac{\partial u}{\partial y} = xy \tag{11}$$

As before, we write the equations

$$\frac{dx}{xu} = \frac{dy}{yu} = \frac{du}{xy} \tag{12}$$

The first part may be written

$$\frac{dx}{x} = \frac{dy}{y}$$

the solution of which is $y = c_1x$; substituting this in the second part, we have

$$\frac{dy}{u} = \frac{c_1dx}{u} = \frac{du}{x}$$

the solution of which is $xy - u^2 = c_2$. The general solution of (11), therefore, is

$$f_3\left[(xy - u^2), \frac{y}{x}\right] = 0 \tag{13}$$

The general methods of solution of partial differential equations are quite incompletely developed. In addition to the method given above for linear partial differential equations of the first order, there are several methods available for certain types of equations, as given by Forsyth and by Mellor.* In general, when such methods fail, resort must be had to trial, possible solutions being tested by differentiation and comparison of the result with the original equation to be solved.

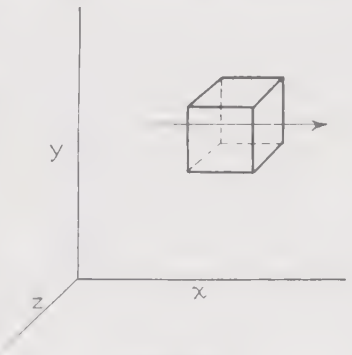

FIG. 52.

97. Setting up a Partial Differential Equation. The procedure in setting up partial differential equations is quite similar to that described in Chap. II for ordinary differential equations. As an example of a differential material balance, consider the unsteady-state flow, through any apparatus, of a noncompressible fluid containing a dissolved solute. Let u_x, u_y, u_z represent the components of velocity in the x, y, and z directions, respectively. Let c represent the concentration of the dissolved solute as weight per unit volume and θ represent time. Consider a differential volume of the apparatus, represented in Fig. 52 by a cube of sides dx, dy, and dz. In the direction indicated by the arrow, the fluid velocity is u_x, and the rate at which solute is brought into the cube is $u_x c\, dy\, dz$. At the opposite face, the rate at which solute leaves the cube is

$$\left[u_x c + \frac{\partial(u_x c)}{\partial x} dx\right] dy\, dz$$

Similar equations apply to the flow in the y and z directions, and

$$\text{Total rate of input} = u_x c\, dy\, dz + u_y c\, dx\, dz + u_z c\, dx\, dy$$

* FORSYTH, "Treatise on Differential Equations," Macmillan & Company, Ltd., London, 1888; MELLOR, "Higher Mathematics," Longmans, Green & Company, New York, 1902.

$$\text{Total rate of output} = \left[u_x c + \frac{\partial(u_x c)}{\partial x}dx\right]dy\,dz + \left[u_y c + \frac{\partial(u_y c)}{\partial y}dy\right]dx\,dz + \left[u_z c + \frac{\partial(u_z c)}{\partial z}dz\right]dy\,dx$$

Also, the

$$\text{Rate of accumulation} = \frac{\partial c}{\partial \theta}dx\,dy\,dz$$

Substitution into the general material balance

$$\text{Input} - \text{output} - \text{accumulation} = 0$$

gives

$$\frac{\partial c}{\partial \theta} + \frac{\partial(u_x c)}{\partial x} + \frac{\partial(u_y c)}{\partial y} + \frac{\partial(u_z c)}{\partial z} = 0 \qquad (14)$$

The material balance in the form of the preceding partial differential equation is a form of the so-called "equation of continuity," of basic importance in hydromechanics.

As another example, consider the drying of air in a batch process by means of a tower packed with a solid lump desiccant such as silica gel. The air to be dried enters at the rate of G lb. per hour (bone-dry basis) per sq. ft. of tower cross section. Let H represent the absolute humidity of the air at any point and ρ its density, expressed as lb. bone-dry air per cu. ft. Let c represent the water content of the silica gel, expressed as lb. moisture per cu. ft. of bulk volume. Consider a differential element dL of the tower, defined by two horizontal planes a differential distance apart. At any time θ the rate at which moisture enters this element in the air stream is GH lb. per hour. The rate at which it leaves at the same time θ is

$$G\left(H + \frac{\partial H}{\partial L}dL\right)$$

Since the two independent variables are taken as L and θ it is understood that θ is held constant in the operation $\partial H/\partial L$. The accumulation is then $-G(\partial H/\partial L)dL$ and must be equal to the depletion of moisture from both air and solid in the differential element. If F represents the fraction voids, then the air contained in the element is $\rho F\,dL$ lb. bone-dry air, and if ρ is taken as constant, the accumulation from the air in the element is $\rho F(\partial H/\partial \theta)dL$. The accumulation in the solid is similarly

$(\partial c/\partial\theta)dL$, and, equating the two expressions for accumulation, we have

$$-G\frac{\partial H}{\partial L}dL = \rho F\frac{\partial H}{\partial \theta}dL + \frac{\partial c}{\partial \theta}dL$$

or

$$G\frac{\partial H}{\partial L} + \rho F\frac{\partial H}{\partial \theta} + \frac{\partial c}{\partial \theta} = 0 \qquad (15)$$

In this particular case, another equation is needed before the problem can be solved, but the derivation of (15) is given as illustrative of the method of setting up equations of this type. The other equation is the differential equation defining the rate of transfer of water vapor from air to solid in terms of H and c, and the solution of the two simultaneous partial differential equations is required. This particular problem is complicated by the fact that the potential causing diffusion is not a simple quantity, since the partial pressure of the water vapor over the solid is related to c by a power function of the Freundlich type. The similar problem for heat transfer from a fluid to a bed of broken solids or balls has been described by Furnas.*

98. Basic Equation for Heat Conduction. Heating or cooling processes in which temperature varies with time are cases of "unsteady-state" heat transfer. Because the laws of heat conduction are well known, it is possible to obtain rigorous solutions to many problems of unsteady-state heat transfer by conduction. The practical aspect of the problem served as an incentive for the development of certain of the mathematics involved in the problems encountered, as illustrated by Fourier's classic work "Théorie analytique de la chaleur," 1822.

The variables to be related are, in general, temperature t, time θ, and position (as given by the coordinates x, y, z), and it is clear that partial differential equations are to be expected. We shall first proceed to follow the method of a differential heat balance to obtain the general differential equation in Cartesian coordinates. Assume the solid to be isotropic, *i.e.*, to have the same properties in all directions, so that the thermal conductivity k, the specific heat C, and the density ρ may be taken as constant and independent of the direction of heat flow. Again on reference

* *Trans. Am. Inst. Chem. Eng.*, **24**, 142 (1930).

to Fig. 52, let the differential cube represent any element in a solid in which heat is being conducted. By Newton's law, the quantity of heat that enters the cube in the direction of the arrow, in time $d\theta$, is

$$-k\frac{\partial t}{\partial x}dy\ dz\ d\theta$$

where the product $dy\ dz$ is the face area normal to the direction of flow. The quantity of heat that leaves the opposite face is

$$-k\left[\frac{\partial t}{\partial x}+\frac{\partial}{\partial x}\left(\frac{\partial t}{\partial x}\right)dx\right]dy\ dz\ d\theta$$

Substitution into a heat balance

$$\text{Input} - \text{output} = \text{accumulation}$$

gives the accumulation of heat in the cube due to flow in the x direction as

$$-k\frac{\partial t}{\partial x}dy\ dz\ d\theta + k\left[\frac{\partial t}{\partial x}+\frac{\partial}{\partial x}\left(\frac{\partial t}{\partial x}\right)dx\right]dy\ dz\ d\theta$$
$$= k\frac{\partial}{\partial x}\left(\frac{\partial t}{\partial x}\right)dx\ dy\ dz\ d\theta = k\frac{\partial^2 t}{\partial x^2}dx\ dy\ dz\ d\theta$$

The heat flow in the y and z directions results in similar terms representing accumulation in the cube, the total of which is

$$k\left(\frac{\partial^2 t}{\partial x^2}+\frac{\partial^2 t}{\partial y^2}+\frac{\partial^2 t}{\partial z^2}\right)dx\ dy\ dz\ d\theta$$

This must be equal to the accumulation of sensible heat content of the cube in time $d\theta$,

$$C\rho\frac{\partial t}{\partial \theta}dx\ dy\ dz\ d\theta$$

where $C\rho\ dx\ dy\ dz$ represents the heat capacity of the element. When the two accumulations are equated

$$\frac{\partial t}{\partial \theta}=\frac{k}{C\rho}\left[\frac{\partial^2 t}{\partial x^2}+\frac{\partial^2 t}{\partial y^2}+\frac{\partial^2 t}{\partial z^2}\right] \tag{16}$$

which is the desired general form. It is sometimes abbreviated by writing

$$\frac{\partial t}{\partial \theta}=\alpha\nabla^2 t \tag{17}$$

where α, termed the thermal diffusivity, is written for $k/C\rho$ and $\nabla^2 t$ is an abbreviation for the three quantities in the square brackets.

This equation has been solved for a large number of practical cases, and the resulting forms are well known. Carslaw* derives and lists most of the cases that are of importance; and his work should be referred to for a full treatment of the subject.

Before proceeding with illustrations of the method of solving (16), we shall consider one more illustration of the derivation of a similar partial differential equation. A fluid is moving at a uniform velocity V in the direction x (in the direction of the arrow of Fig. 52). Heat is suddenly liberated at a fixed point in the stream and the heat liberation continued at a steady rate. Again on the basis of the differential cube, the heat entering one face in time $d\theta$, due both to the conduction in the x direction and to the sensible heat carried by the stream, is

$$C\rho Vt\, dy\, dz\, d\theta - k\frac{\partial t}{\partial x} dy\, dz\, d\theta$$

where sensible heat is calculated above the arbitrary datum $t = 0$. In the same time $d\theta$, the heat leaving the opposite face by both mechanisms is

$$\left[\left(C\rho Vt + C\rho V\frac{\partial t}{\partial x}dx\right) - k\left(\frac{\partial t}{\partial x} + \frac{\partial^2 t}{\partial x^2}dx\right)\right] dy\, dz\, d\theta$$

The accumulation of heat within the cube is, therefore,

$$-\left(C\rho V\frac{\partial t}{\partial x} - k\frac{\partial^2 t}{\partial x^2}\right) dx\, dy\, dz\, d\theta$$

Following the method of the previous illustration, the accumulation within the cube by conduction in the y and z directions is

$$k\left(\frac{\partial^2 t}{\partial y^2} + \frac{\partial^2 t}{\partial z^2}\right) dx\, dy\, dz\, d\theta$$

The sum of the last two quantities is equated to the accumulation of sensible heat within the cube as expressed by its change in temperature:

$$C\rho\frac{\partial t}{\partial \theta} dx\, dy\, dz\, d\theta$$

* "Mathematical Theory of the Conduction of Heat in Solids," The Macmillan Company, New York, 1921.

whence

$$C\rho\frac{\partial t}{\partial \theta} = k\left(\frac{\partial^2 t}{\partial x^2} + \frac{\partial^2 t}{\partial y^2} + \frac{\partial^2 t}{\partial z^2}\right) - C\rho V\frac{\partial t}{\partial x} \tag{18}$$

Eventually a steady state is reached, when the temperature is a function only of position and not of time. $\partial t/\partial\theta$ will be zero, and the equation reduces to

$$V\frac{\partial t}{\partial x} = \alpha\nabla^2 t \tag{19}$$

99. Infinite Slab. Probably the most instructive example of the solution of the general equation for heat conduction is the case of an infinite slab. The problem is to find a solution of the differential equation (16) which, at the same time, will satisfy certain other conditions imposed in defining the problem. Suppose an infinite slab (extending indefinitely in the y and z directions) at an initial temperature t_1 has its two faces suddenly cooled to t_0; what is the relation between temperature, time after quenching, and position within the slab?

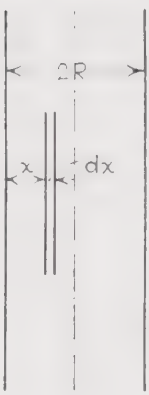

FIG. 53.—Infinite slab.

The origin is placed at one face with the other face at $x = 2R$, as shown in Fig. 53. (By experience, it is found that the problem is more difficult if the origin is placed in the center of the slab.) Heat is lost at the two faces, and, since the solid extends indefinitely in the y and z directions, it is apparent that heat flows only in the x direction. Consequently, $\partial^2 t/\partial y^2$ and $\partial t^2/\partial z^2$ are zero, and (16) reduces to

$$\frac{\partial t}{\partial \theta} = \alpha\frac{\partial^2 t}{\partial x^2} \tag{20}$$

The conditions imposed by the statement of the problem, termed the "boundary conditions," are

$$t = t_1 \quad \text{at} \quad \theta = 0 \tag{21}$$
$$t = t_0 \quad \text{at} \quad \theta = \infty \tag{22}$$
$$t = t_0 \quad \text{at} \quad x = 0 \tag{23}$$
$$t = t_0 \quad \text{at} \quad x = 2R \tag{24}$$

In order to simplify the first two conditions, replace t by the variable Δ, defined as

$$\Delta = \frac{t - t_0}{t_1 - t_0} \tag{25}$$

whence (20) becomes

$$\frac{\partial \Delta}{\partial \theta} = \alpha \frac{\partial^2 \Delta}{\partial x^2} \tag{26}$$

Note that Δ is defined as the unaccomplished cooling at any point divided by the total possible cooling and must vary from 1 to 0. The conditions are now

$$\Delta = 1 \quad \text{at} \quad \theta = 0 \tag{27}$$
$$\Delta = 0 \quad \text{at} \quad \theta = \infty \tag{28}$$
$$\Delta = 0 \quad \text{at} \quad x = 0 \tag{29}$$
$$\Delta = 0 \quad \text{at} \quad x = 2R \tag{30}$$

It is desired to find a solution of (26) that also satisfies (27), (28), (29), and (30).

In solving (26), a device is employed, which is frequently useful for such equations. Assume that Δ may be represented by the product $X\Theta$, where X is defined as a function of x only, independent of θ, and Θ is defined as a function of θ only, independent of x. Substituting in (26) gives

$$X \frac{\partial \Theta}{\partial \theta} = \alpha \Theta \frac{\partial^2 X}{\partial x^2}$$

or

$$\frac{1}{X} \frac{\partial^2 X}{\partial x^2} = \frac{1}{\alpha \Theta} \frac{\partial \Theta}{d\theta} \tag{31}$$

Now by definition, Θ is independent of x; so, as x varies, the right-hand side of the equation remains constant. Similarly, the left-hand side remains constant as θ varies, and both sides must be considered as constant. Representing this constant by $-a^2$, we have the two equations

$$\frac{1}{X} \frac{d^2 X}{dx^2} = -a^2 \tag{32}$$

$$\frac{1}{\alpha \Theta} \frac{d\Theta}{d\theta} = -a^2 \tag{33}$$

which are ordinary differential equations since but two variables are involved in each. These may be solved separately to give

$$X = c_1 \cos ax + c_2 \sin ax$$

and

$$\Theta = c_3 e^{-\alpha a^2 \theta}$$

which may be checked by differentiating and comparing with (32) and (33). The indicated solution is

$$\Delta = X\Theta = c_3 e^{-\alpha a^2 \theta}(c_1 \cos ax + c_2 \sin ax) \tag{34}$$

This clearly satisfies (28) and may be made to satisfy (29) if we let $c_1 = 0$. The solution reduces to

$$\Delta = c_4 e^{-\alpha a^2 \theta} \sin ax \tag{35}$$

which is true for any value of θ after the start of the cooling. Substituting condition (30) for an infinitely small value of θ yields

$$0 = c_4 \sin 2aR \tag{36}$$

which is true if $a = n\pi/2R$, where n is an integer.
We have now arrived at the solution

$$\Delta = c_4 e^{-\alpha \frac{n^2\pi^2}{4R^2}\theta} \sin \frac{n\pi x}{2R} \tag{37}$$

and have yet to satisfy (27). This is more difficult, since it is not simply the evaluation of c_4; we cannot visualize the temperature distribution in the slab at small values of θ as being represented by a sine curve. The solution (34) is valid for any positive value of a; and (37) is valid for any positive value of n, such as $n = 1$, $n = 2$. But the original Eq. (26) is a linear differential equation, and the sum of any number of solutions is also a solution. Consequently, if the expressions (37), each with a different value of n, are added, the resulting sum is also a solution of (26), and we write

$$\Delta = A_1 e^{-\frac{\alpha\pi^2\theta}{4R^2}} \sin \frac{\pi x}{2R} + A_2 e^{-\frac{4\alpha\pi^2\theta}{4R^2}} \sin \frac{2\pi x}{2R} + A_3 e^{-\frac{9\alpha\pi^2\theta}{4R^2}} \sin \frac{3\pi x}{2R} + \cdots \tag{38}$$

where A_1, A_2, etc., are constants. Now applying condition (27) we have

$$1 = A_1 \sin \frac{\pi x}{2R} + A_2 \sin \frac{2\pi x}{2R} + A_3 \sin \frac{3\pi x}{2R} + \cdots \tag{39}$$

and the general constant A_n may be determined by comparing this series term by term with a Fourier series for 1 in the interval 0 to $2R$. This is written

$$1 = \frac{4}{\pi}\left[\sin\frac{\pi x}{2R} + \frac{1}{3}\sin\frac{3\pi x}{2R} + \frac{1}{5}\sin\frac{5\pi x}{2R} + \cdots\right] \tag{40}$$

This is obtained by setting up a Fourier series for the odd function $f(x) = -1$ from $-2R$ to 0 and $f(x) = 1$ from 0 to $2R$, following

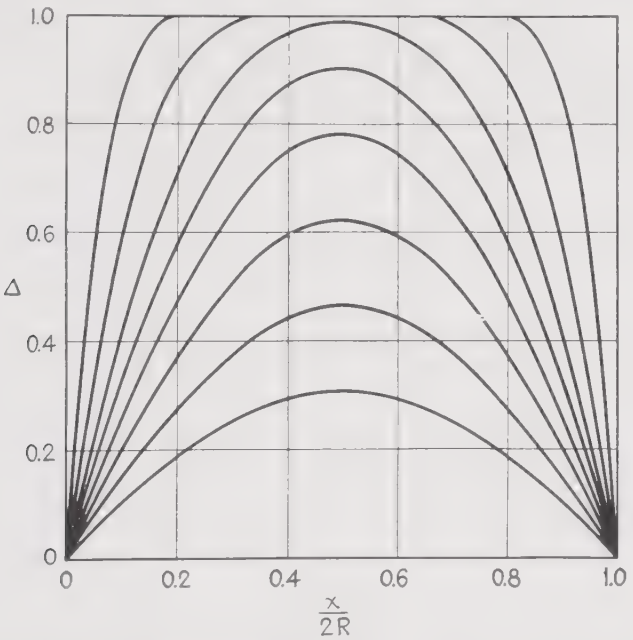

FIG. 54.—Temperature distribution in infinite slab.

the methods described in Chap. IV. When (39) and (40) are compared, it is apparent that A_n is $4/n\pi$ where n is odd only and that it may be written

$$A_n = [1 - (-1)^n]\frac{2}{n\pi}$$

Substituting in (38), we obtain the final result

$$\Delta = \frac{4}{\pi}\left[e^{-\left(\frac{\pi}{2}\right)^2\tau}\sin\frac{\pi x}{2R} + \frac{1}{3}e^{-9\left(\frac{\pi}{2}\right)^2\tau}\sin\frac{3\pi x}{2R} + \frac{1}{5}e^{-25\left(\frac{\pi}{2}\right)^2\tau}\sin\frac{5\pi x}{2R} + \cdots\right] \tag{41}$$

where $\tau = \alpha\theta/R^2$. Figure 54 shows a plot of the results as Δ vs. $x/2R$ for several values of τ. As τ increases, the series

converges more and more rapidly, until in the vicinity of $\tau = 0.5$ the first term only is of importance and the temperature function is represented by a sine curve.

The total heat content of the slab is the integral of the temperature-heat capacity product. If we define E as the ratio of the sensible heat content above the datum temperature t_0 to the heat that is lost in cooling the whole slab from t_1 to t_0, then

$$E = \frac{1}{2R}\int_0^{2R} \Delta \, dx \tag{42}$$

This is easily obtained by integrating (41) term by term, with the result

$$E = \frac{8}{\pi^2}\left(e^{-\left(\frac{\pi}{2}\right)^2\tau} + \frac{1}{9}e^{-9\left(\frac{\pi}{2}\right)^2\tau} + \frac{1}{25}e^{-25\left(\frac{\pi}{2}\right)^2\tau} + \cdots\right) \tag{43}$$

When τ is greater than about 0.5, this reduces to

$$\ln E = \ln \frac{8}{\pi^2} - \frac{\pi^2}{4}\tau \tag{44}$$

suggesting a straight line on semilog coordinate paper.

100. Infinite Slab with Nonuniform Initial Temperature Distribution. As an extension of this problem, consider the case where the initial temperature is not constant at t_1 through the slab but is represented by any function $f(x)$ of the position. In order to avoid confusion, use $f(x')$ to distinguish between position with reference to the original temperature function and the principal variable x with which subsequent temperatures are associated. The procedure in the solution is the same as before down to the evaluation of the constants in (38).

Since there is no longer a single value for the total possible temperature change $(t_1 - t_0)$, a new variable γ will be defined as $t - t_0$. The differential expression (26) still holds if γ replaces Δ, as do conditions (28), (29), and (30). Condition (27) is now $\gamma = f(x')$ at $\theta = 0$; so we set up a Fourier series in sine terms for $f(x')$ instead of for 1.

$$f(x') = \frac{1}{R}\left[\sin\frac{\pi x}{2R}\int_0^{2R} f(x')\sin\frac{\pi x'}{2R}dx' + \sin\frac{2\pi x}{2R}\int_0^{2R} f(x')\right.$$
$$\left.\sin\frac{2\pi x'}{2R}dx' + \sin\frac{3\pi x}{2R}\int_0^{2R} f(x')\sin\frac{3\pi x'}{2R}dx' + \cdots\right] \tag{45}$$

By comparison with (39) [when 1 is replaced by $f(x')$ on the left] it is apparent that

$$A_n = \frac{1}{R}\int_0^{2R} f(x') \sin \frac{n\pi x'}{2R} dx'$$

whence

$$\gamma = \frac{1}{R}\left[e^{-\left(\frac{\pi}{2}\right)^2 \tau} \sin \frac{\pi x}{2R} \int_0^{2R} f(x') \sin \frac{\pi x'}{2R} dx' + e^{-4\left(\frac{\pi}{2}\right)^2 \tau} \sin \frac{2\pi x}{2R} \right.$$
$$\int_0^{2R} f(x') \sin \frac{2\pi x'}{2R} dx' + e^{-9\left(\frac{\pi}{2}\right)^2 \tau} \sin \frac{3\pi x}{2R} \int_0^{2R} f(x') \sin \frac{3\pi x'}{2R} dx'$$
$$\left. + \cdots \right] \quad (46)$$

which may be written

$$\gamma = \frac{1}{R} \sum_{n=1}^{n=\infty} e^{-n^2\left(\frac{\pi}{2}\right)^2 \tau} \sin \frac{n\pi x}{2R} \int_0^{2R} f(x') \sin \frac{n\pi x'}{2R} dx' \quad (47)$$

This is easily shown to reduce to (41) for $f(x') = (t_1 - t_0)$ since

$$\int_0^{2R} \sin \frac{n\pi x'}{2R} dx' = [1 - (-1)^n] \frac{2R}{n\pi}$$

Although the examples given, as well as the standard reference books such as Carslaw, discuss the solutions of (16) as applied to heat conduction, it is apparent that the results are equally valid for any case to which (16) may be applied. This is true, for example, of unsteady-state diffusion in stagnant gases, and the solution for the infinite slab has been applied with some success to the drying of slow-drying solids, where the rate of drying is limited by the rate at which water can diffuse to the surface.

101. Interdiffusion of Two Gases. The diffusivity for a binary gas mixture has been obtained experimentally by measuring the rate of interdiffusion of two gases originally confined in the two ends of a hollow cylinder. A thin diaphragm separating the gases at the center is suddenly removed and the gas allowed to diffuse for a measured time. The diaphragm is then replaced, and the gases in each half of the cylinder are well mixed and analyzed. In the absence of convection effects, the molecular diffusivity is obtained by comparing the result with a solution of the basic differential equation. For this case, the equation is

$$\frac{\partial p}{\partial \theta} = D\frac{\partial^2 p}{\partial x^2} \tag{48}$$

where p represents the partial pressure of one gas and D is the diffusivity.

In the solution of (48), the first scheme is to replace p by some variable that will vary from 1 to 0 as θ increases from zero to infinity. If the two halves of the cylinder are identical, p will vary between the limits of p_0 and p_0 2. Choose a new variable P, therefore, such that

$$P = 2\left(\frac{p}{p_0} - \frac{1}{2}\right)$$

The constants disappear on differentiating, and (48) becomes

$$\frac{\partial P}{\partial \theta} = D\frac{\partial^2 P}{\partial x^2}$$

If the gases are pure and at the same pressure p_0 in both halves at the start, then the concentrations will be symmetrical about the mid-point, and it is necessary to obtain a solution only for one half. Place the origin at the center, and let the length of the cylinder be $2R$. Then the conditions are

$$P = 1 \quad \text{at} \quad \theta = 0 \tag{49}$$

$$P = 0 \quad \text{at} \quad \theta = \infty \tag{50}$$

$$P = 0 \quad \text{at} \quad x = 0 \tag{51}$$

$$\frac{\partial P}{\partial x} = 0 \quad \text{at} \quad x = R \tag{52}$$

The last is arrived at by considering that there is no diffusion across the plane representing the end of the cylinder and, therefore, no gradient of P with x. The solution of the equation is obtained by the method outlined previously, as

$$P = C_3 e^{-Da^2\theta}(C_1 \cos ax + C_2 \sin ax) \tag{53}$$

From (51), it follows that $C_1 = 0$. From (52), if θ is assumed finite,

$$\cos aR = 0, \qquad \text{and} \qquad a = \frac{(2n-1)\pi}{2R}$$

Adding solutions for integral values of n and substituting (49), we have

$$1 = A_1 \sin \frac{\pi x}{2R} + A_2 \sin \frac{3\pi x}{2R} + A_3 \sin \frac{5\pi x}{2R} + \cdots \tag{54}$$

which is compared with (40) to obtain

$$A_n = \frac{4}{\pi(2n-1)}; \qquad \text{or} \qquad A_n = [1-(-1)^n]\frac{2}{n\pi}$$

and the resulting solution is

$$P = \frac{4}{\pi}\left(e^{-\left(\frac{\pi}{2}\right)^2\frac{D\theta}{R^2}}\sin\frac{\pi x}{2R} + \frac{1}{3}e^{-9\left(\frac{\pi}{2}\right)^2\frac{D\theta}{R^2}}\sin\frac{3\pi x}{2R} + \cdots\right) \tag{55}$$

which is essentially identical with the solution (41) for heat conduction in an infinite slab.

If F represents the fraction of the original gas left in one-half of the cylinder,

$$F = \frac{1}{2} + \frac{1}{2R}\int_0^R P\,dx = \frac{1}{2} + \frac{4}{\pi^2}\left(e^{-\left(\frac{\pi}{2}\right)^2\frac{D\theta}{R^2}} + \frac{1}{9}e^{-9\left(\frac{\pi}{2}\right)^2\frac{D\theta}{R^2}} + \frac{1}{25}e^{-25\left(\frac{\pi}{2}\right)^2\frac{D\theta}{R^2}} + \cdots\right) \tag{56}$$

This function has been plotted by Smith* for use in estimating the time of standing necessary for a prepared gas mixture in a pressure cylinder to attain various degrees of uniformity.

102. Infinite Cylinder. The solution of Eq. (16) for the case of conduction or diffusion in a cylinder of infinite length follows a procedure similar to that followed in obtaining a solution for the slab but involves the use of an infinite series of Bessel functions in place of a Fourier series.

Conduction in a cylinder involves two-dimensional heat flow, and a fourth variable is introduced. Since the cylinder is assumed to be of infinite length, there is no heat flow along the axis (in the x direction), $\partial^2 t\ \partial x^2$ is zero, and (16) reduces to

$$\frac{\partial t}{\partial \theta} = \alpha\left(\frac{\partial^2 t}{\partial y^2} + \frac{\partial^2 t}{\partial z^2}\right) \tag{57}$$

Since the cylinder is symmetrical about its axis, one variable may be eliminated by changing to cylindrical coordinates. This change was shown in Par. 76 to give

$$\frac{\partial t}{\partial \theta} = \alpha\left(\frac{\partial^2 t}{\partial r^2} + \frac{1}{r}\frac{\partial t}{\partial r} + \frac{1}{r^2}\frac{\partial^2 t}{\partial \phi^2} + \frac{\partial^2 t}{\partial x^2}\right) \tag{58}$$

* *Ind. Eng. Chem.*, **26**, 1167 (1934).

Although (58) is ordinarily obtained from (16) by this method, it may also be obtained directly by considering heat conduction in a differential element of the cylinder. Its derivation in this way will serve as an additional illustration of the general method of setting up partial differential equations.

Referring to Fig. 55, consider the differential element $da\ dr\ dx$ of a cylinder, where r is the radial distance of any point from the axis, ϕ is the angle of the radius with reference to a fixed plane through the axis, x is the distance along the axis, and da is the length of the differential arc $r\ d\phi$. Following the usual procedure of a differential heat balance on the element of the solid indicated, we have, for the x direction, a rate of heat flow

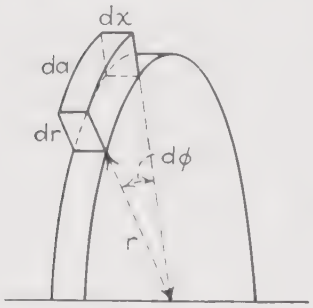

FIG. 55.

$$-k\frac{\partial t}{\partial x}dr\ da, \text{ at } x,$$

and

$$-k\left(\frac{\partial t}{\partial x} + \frac{\partial^2 t}{\partial x^2}dx\right)dr\ da, \text{ at } x + dx$$

The accumulation, or input minus output, is $k(\partial^2 t/\partial x^2)dx\ dr\ da$. In the radial direction, at r, the rate of heat input to the element is

$$-k\frac{\partial t}{\partial r}dx\ da = -k\frac{\partial t}{\partial r}r\ dx\ d\phi$$

and the heat conducted out at $r + dr$ is

$$-k\left(\frac{\partial t}{\partial r} + \frac{\partial^2 t}{\partial r^2}dr\right)(r + dr)d\phi\ dx$$

Note that $(r + dr)d\phi$ replaces da. The accumulation is

$$k\left[r\frac{\partial^2 t}{\partial r^2}dr + \frac{\partial t}{\partial r}dr + \frac{\partial^2 t}{\partial r^2}(dr)^2\right]d\phi\ dx$$

When the second-order differential is neglected, this becomes

$$k\left(r\frac{\partial^2 t}{\partial r^2} + \frac{\partial t}{\partial r}\right)dr\ d\phi\ dx = k\left(\frac{\partial^2 t}{\partial r^2} + \frac{1}{r}\frac{\partial t}{\partial r}\right)da\ dr\ dx$$

Now at ϕ, the heat conducted in the circumferential direction is

$$-k\frac{\partial t}{\partial a}dr\ dx$$

and at $(\phi + d\phi)$ it is

$$-k\left(\frac{\partial t}{\partial a} + \frac{\partial^2 t}{\partial a^2}da\right)dr\,dx$$

giving the accumulation

$$k\frac{\partial^2 t}{\partial a^2}da\,dr\,dx = \frac{1}{r^2}\frac{\partial^2 t}{\partial \phi^2}da\,dr\,dx$$

Equating the total accumulation due to heat flow in the three directions to the change in sensible heat content of the element results in

$$C\rho\frac{\partial t}{\partial \theta}da\,dr\,dx = k\left(\frac{\partial^2 t}{\partial x^2} + \frac{\partial^2 t}{\partial r^2} + \frac{1}{r}\frac{\partial t}{\partial r} + \frac{1}{r^2}\frac{\partial^2 t}{\partial \phi^2}\right)da\,dr\,dx$$

or

$$\frac{\partial t}{\partial \theta} = \alpha\left(\frac{\partial^2 t}{\partial x^2} + \frac{\partial^2 t}{\partial r^2} + \frac{1}{r}\frac{\partial t}{\partial r} + \frac{1}{r^2}\frac{\partial^2 t}{\partial \phi^2}\right)$$

which is identical with (58).

In the problem of heat conduction in a cylinder, there may or may not be radial symmetry with respect to temperature, depending on whether or not the initial temperature distribution is symmetrical about the axis. In order to simplify the problem, we shall assume the initial temperature to be a function of r only, expressed by $f(r)$. The whole surface is suddenly cooled to t_0, and at any subsequent time the temperatures will be symmetrical about the axis of the cylinder, and $\partial^2 t/\partial \phi^2$ will be zero. Because the cylinder is taken to be of infinite length, it is clear that the term $\partial^2 t/\partial x^2$ also drops out.

The problem, therefore, is to solve the equation

$$\frac{\partial t}{\partial \theta} = \alpha\left(\frac{\partial^2 t}{\partial r^2} + \frac{1}{r}\frac{\partial t}{\partial r}\right) \tag{59}$$

As before, define γ as $t - t_0$ so as to make the boundary conditions simpler without changing the differential equation. As t varies with time from t_1 to t_0, γ varies from $f(r)$ to 0. The boundary conditions, therefore, are

$$\gamma = f(r) \quad \text{at} \quad \theta = 0 \tag{60}$$

$$\gamma = 0 \quad \text{at} \quad \theta = \infty \tag{61}$$

$$\gamma = 0 \quad \text{at} \quad r = R \tag{62}$$

The procedure at the start is similar to that followed in the solution of the equation for the infinite slab. Assume $\gamma = \Phi \cdot \Theta$,

where Φ is taken to be a function of r only and Θ is a function of θ only. Substituting in (59) yields

$$\Phi\frac{\partial\Theta}{\partial\theta} = \alpha\left(\Theta\frac{\partial^2\Phi}{\partial r^2} + \frac{\Theta}{r}\frac{\partial\Phi}{\partial r}\right)$$

or

$$\frac{1}{\alpha\Theta}\frac{\partial\Theta}{\partial\theta} = \frac{1}{\Phi}\frac{\partial^2\Phi}{\partial r^2} + \frac{1}{r\Phi}\frac{\partial\Phi}{\partial r} \tag{63}$$

The left side is independent of r and will not vary as r varies; the right side is independent of θ and will not change as θ is varied. Each side may be set equal to the constant $-a^2$ and the separate ordinary differential equations obtained.

$$\frac{d\Theta}{d\theta} + a^2\alpha\Theta = 0 \tag{64}$$

and

$$\frac{d^2\Phi}{dr^2} + \frac{1}{r}\frac{d\Phi}{dr} + a^2\Phi = 0 \tag{65}$$

The solution of the first was obtained previously as

$$\Theta = C_1e^{-a^2\alpha\theta}$$

and the second, after it is multiplied by r^2, is seen to be similar to (60) of Chap. V.

$$x^2\frac{d^2y}{dx^2} + x\frac{dy}{dx} + (x^2 - n^2)y = 0$$

If $y = \Phi$, $n = 0$, and $x = ar$, this becomes identical with (65), and a solution is $J_0(ar)$. The solution of (59) is indicated as

$$\gamma = C_1e^{-a^2\alpha\theta}J_0(ar) \tag{66}$$

We may arbitrarily elect to add a number of such solutions, each with a different value of a, and still have a valid solution, since the equation is linear with the right-hand side equal to zero. We have

$$\gamma = \sum_{n=1}^{n=\infty} A_ne^{-a_n^2\alpha\theta}J_0(a_nr) \tag{67}$$

where we take n as a positive integer. From (62),

$$J_0(a_nR) = 0 \tag{68}$$

which defines a_n. The Bessel function $J_0(x)$ oscillates about the x axis for positive values of x, and (68) consequently has a number of positive roots. The constant a_n is fixed by the relation that a_nR is the nth positive root of (68). It is now necessary only to evaluate A_n. In the case of the slab, this was done by comparing the series with a known series. The procedure is similar in this case, but the series is a series of Bessel functions instead of a Fourier series. By (60) and (67),

$$f(r) = A_1J_0(a_1r) + A_2J_0(a_2r) + A_3J_0(a_3r) + \cdots \tag{69}$$

and A_n may be obtained by comparison of this series with an expansion of $f(r)$ in terms of a series of Bessel functions of this type. Byerly* gives formulas by which this may be done. In a case such as the foregoing, where a_nR is the nth positive root (R is a constant) of $J_0(a_nR) = 0$, an expression $f(r)$ may be expanded.

$$f(r) = \sum_{n=1}^{n=\infty} \frac{2J_0(a_nr)}{R^2[J_1(a_nR)]^2} \int_0^R rf(r)J_0(a_nr)dr \tag{70}$$

This is compared with (69), whence A_n is obvious, and (67) is written

$$\gamma = \frac{2}{R^2} \sum_{n=1}^{n=\infty} \frac{e^{-a_n^2\alpha\theta}J_0(a_nr)}{[J_1(a_nR)]^2} \int_0^R rf(r)J_0(a_nr)dr \tag{71}$$

To use this, it is necessary to have tables of $J_0(x)$, $J_1(x)$, and of the positive roots of $J_0(x)$. The integration involved in each term is carried out using the initial $f(r)$ and results in a different constant for each term. If $f(r) = 1$,

$$\int_0^R rJ_0(a_nr)dr = \frac{1}{a_n^2} \int_0^{a_nR} xJ_0(x)dx = \frac{R}{a_n}J_1(a_nR)$$

This relation may be obtained by integrating the series for $J_0(x)$ term by term. The resulting solution for the case of $f(r) = 1$ is

$$\gamma = \frac{2}{R} \sum_{n=1}^{n=\infty} \frac{e^{-a_n^2\alpha\theta}J_0(a_nr)}{a_nJ_1(a_nR)} \tag{72}$$

* "Fourier Series and Spherical Harmonics," p. 229. Ginn and Company, Boston, 1893.

where, as before, a_nR is the nth positive root of $J_0(a_nR) = 0$. The temperature function γ has now been made 1 at the start; so Δ will now be defined as

$$\Delta = \frac{t - t_0}{t_1 - t_0}$$

to give the limiting values of 1 and 0; t_1 is the initial uniform temperature. It follows that γ may be replaced by Δ in (72).

103. Constant-rate Drying of an Infinite Slab. Carslaw's book* gives the solutions for a large variety of heat conduction problems, many of which may be used for analogous problems of diffusion. Many of the solutions given may be adapted to other boundary conditions and the solution for the case in hand obtained with less effort.

As an example, consider the problem of evaluating the moisture distribution in an infinite slab being dried at a constant rate of β lb. (hr.)(sq. ft.) from both faces. Assume the rate of moisture movement in the solid to be proportional to the moisture gradient, whence it follows that the basic differential equation (20) applies. If C represents the moisture concentration as lb. water per cu. ft. bulk volume and α is the diffusion coefficient of water through the solid, then

$$\frac{\partial C}{\partial \theta} = \alpha \frac{\partial^2 C}{\partial x^2} \tag{73}$$

Let the initial moisture concentration be C_1 and be uniform through the slab. The boundary conditions are

$$C = C_1 \qquad \text{at} \qquad \theta = 0 \tag{74}$$

$$\alpha \frac{\partial C}{\partial x} = \beta \qquad \text{at} \qquad x = 0 \tag{75}$$

$$\alpha \frac{\partial C}{\partial x} = -\beta \qquad \text{at} \qquad x = 2R \tag{76}$$

This case is not treated by Carslaw. However, if a change of variables is made, letting $\partial C/\partial x = p$, then from (73),

$$\frac{\partial^2 C}{\partial \theta \, \partial x} = \alpha \frac{\partial^3 C}{\partial x^3}$$

$$\frac{\partial p}{\partial \theta} = \alpha \frac{\partial^2 p}{\partial x^2} \tag{77}$$

* *Loc. cit.*

The differential equation is not changed in form, but the boundary conditions are now

$$p = 0 \qquad \text{at} \qquad \theta = 0 \tag{78}$$

$$p = \frac{\beta}{\alpha} \qquad \text{at} \qquad x = 0 \tag{79}$$

$$p = -\frac{\beta}{\alpha} \qquad \text{at} \qquad x = 2R \tag{80}$$

Carslaw gives the solution for this case when $p = f(x')$ at $\theta = 0$ as

$$p = \frac{\beta}{\alpha} - \frac{\beta x}{\alpha R} - \frac{2}{\pi}\sum_{n=1}^{n=\infty} \frac{\frac{\beta}{\alpha}\cos n\pi + \frac{\beta}{\alpha}}{n} e^{-n^2\left(\frac{\pi}{2}\right)^2\frac{\alpha\theta}{R^2}} \sin\frac{n\pi x}{2R}$$
$$+ \frac{1}{R}\sum_{n=1}^{n=\infty} C e^{-n^2\left(\frac{\pi}{2}\right)^2\frac{\alpha\theta}{R^2}} \sin\frac{n\pi x}{2R}\int_0^{2R} f(x')\sin\frac{n\pi x'}{2R}dx' \tag{81}$$

Differentiating with respect to x gives

$$\frac{\partial p}{\partial x} = -\frac{\beta}{\alpha R} - \frac{1}{R}\sum_{n=1}^{n=\infty}\frac{\beta}{\alpha}(\cos n\pi + 1)e^{-n^2\left(\frac{\pi}{2}\right)^2\frac{\alpha\theta}{R^2}}\cos\frac{n\pi x}{2R}$$
$$+ \frac{\pi}{2R^2}\sum_{n=1}^{n=\infty} n C e^{-n^2\left(\frac{\pi}{2}\right)^2\frac{\alpha\theta}{R^2}}\cos\frac{n\pi x}{2R}\int_0^{2R} f(x')\sin\frac{n\pi x'}{2R}dx'$$

But $\dfrac{\partial C}{\partial\theta} = \alpha\dfrac{\partial p}{\partial x}$

whence

$$C = \alpha\int\frac{\partial p}{\partial x}d\theta + f(x) = -\frac{\beta\theta}{R} + \frac{4R}{\pi^2}\sum_{n=1}^{n=\infty}\frac{\beta}{\alpha n^2}(\cos n\pi + 1)$$
$$e^{-n^2\left(\frac{\pi}{2}\right)^2\frac{\alpha\theta}{R^2}}\cos\frac{n\pi x}{2R} - \frac{2}{\pi}\sum_{n=1}^{n=\infty}\frac{1}{n}e^{-n^2\left(\frac{\pi}{2}\right)^2\frac{\alpha\theta}{R^2}}\cos\frac{n\pi x}{2R}\int_0^{2R} f(x')$$
$$\sin\frac{n\pi x'}{2R}dx' + f(x) \tag{82}$$

and since the initial moisture distribution is uniform,

$$p = f(x') = 0$$

at $\theta = 0$, and the third term of (82) drops out. When (74) is applied,

$$C_1 = f(x) + \frac{4R\beta}{\alpha\pi^2}\sum_{n=1}^{n=\infty}\frac{1}{n^2}(\cos n\pi + 1)\cos\frac{n\pi x}{2R} = f(x) +$$

$$\frac{4R\beta}{\alpha\pi^2}\sum_{n=1}^{n=\infty}\frac{1}{n^2}[1 + (-1)^n]\cos\frac{n\pi x}{2R} = f(x) + \frac{8R\beta}{\alpha\pi^2}\left(\frac{1}{2^2}\cos\frac{2\pi x}{2R} + \frac{1}{4^2}\cos\frac{4\pi x}{2R} + \frac{1}{6^2}\cos\frac{6\pi x}{2R} + \cdots\right) = f(x) - \frac{\beta}{2\alpha R}\left[2xR - \frac{2}{3}R^2 - x^2\right] \quad (83)$$

The last follows* from the two cosine series (Peirce, Nos. 810 and 812)

$$\frac{\pi^2}{8R}(R - x) = \cos\frac{\pi x}{2R} + \frac{1}{3^2}\cos\frac{3\pi x}{2R} + \frac{1}{5^2}\cos\frac{5\pi x}{2R} + \cdots \quad (84)$$

and

$$\frac{\pi^2}{16R^2}\left(\frac{4R^2}{3} - x^2\right) = \cos\frac{\pi x}{2R} - \frac{1}{2^2}\cos\frac{2\pi x}{2R} + \frac{1}{3^2}\cos\frac{3\pi x}{2R} - \frac{1}{4^2}\cos\frac{4\pi x}{2R} + \cdots \quad (85)$$

Solving (83) for $f(x)$ and substituting in (82), the final result becomes

$$C = C_1 + \frac{\beta}{2\alpha R}\left[2xR - \frac{2}{3}R^2 - x^2 - 2\alpha\theta\right] + \frac{4R\beta}{\pi^2\alpha}\sum_{n=1}^{n=\infty}\frac{1}{n^2}(-1^n + 1)\, e^{-n^2\left(\frac{\pi}{2}\right)^2\frac{\alpha\theta}{R^2}}\cos\frac{n\pi x}{2R} \quad (86)$$

where the constant of integration C_1 represents the initial moisture concentration throughout the slab. It will be observed that, as θ increases, the importance of the series becomes less and the concentration distribution is approximated by a simple parabola. In any actual drying, C cannot be negative, and

* In addition to simplifying the result, this substitution has the advantage of introducing a function of x which does not have discontinuities. Unless this change is made the solution does not satisfy (79) and (80).

the range of values of θ for which (86) may be applied is definitely limited.

The validity of (86) as a solution may be checked by differentiation and comparison with the original differential equation (73) as well as with the boundary conditions (74), (75), and (76).

104. Miscellaneous Shapes and Boundary Conditions. Heat conduction in various other shapes, such as the sphere, may be treated by similar procedures, although the solutions in many cases are more involved than those presented above. The heating or cooling from one face of a thick slab may be treated approximately by the equation for a "semi-infinite solid," defined as one having an infinite thickness and one plane surface of infinite extent. The solution in this case is not particularly difficult and does not involve an infinite series. For the case of a brick-shaped solid (rectangular parallelepiped) of sides $2R_1$, $2R_2$, and $2R_3$, Newman* has shown that the value of Δ for any τ is the product of the three Δ's obtained from the slab equation (41) for three infinite slabs of thickness $2R_1$, $2R_2$, and $2R_3$ for the same θ.† Thus Δ for a point located at distances x_1, x_2, and x_3 in such a shape is the product $(\Delta_1) \cdot (\Delta_2) \cdot (\Delta_3)$, where Δ_1 is obtained from the slab equation by substitution of $x = x_1$ and $R = R_1$, Δ_2 by substitution of $x = x_2$ and $R = R_2$, and Δ_3 by substitution of $x = x_3$ and $R = R_3$. Newman also shows that a similar rule holds for a finite cylinder, where Δ for any point at a radius r and a distance x from one square end is the product of $(\Delta_1) \cdot (\Delta_2)$, where Δ_1 is obtained by substitution of $r = r$ and $R = R_1$ in Eq. (72) for the cylinder, and Δ_2 is obtained for the same θ by substitution of $x = x$ and $R = R_2$ in Eq. (41) for the infinite slab. R_1 is the radius of the finite cylinder, and R_2 is half its length. The same rules apply to E as to Δ, where E represents the integration for total heat content.

The illustrative examples for the infinite slab and the infinite cylinder assumed that the surface was cooled (or heated) instantly to some constant fixed temperature t_0. In the physical case, this corresponds to quenching the solid in a cooling medium at t_0 provided that the surface coefficient of heat transfer from

* *Trans. Am. Inst. Chem. Eng.*, **27**, 310 (1931).

† A point in the solid is located by its perpendicular distances x_1, x_2, and x_3 from the faces of the solid. For example, if the distance between two parallel faces is $2R_1$, x_1 is the perpendicular distance of the point from one of these faces.

surface to fluid was infinite so that there would be no temperature difference between the surface and the fluid. In practice, the surface coefficient is finite, and the surface temperature falls off more or less gradually, approaching the temperature of the surrounding fluid as a limit. To allow for this, it is necessary to rewrite the boundary conditions. If the surface coefficient is h, the surface temperature t_s, and the temperature of the surrounding fluid t_0, then by a heat balance on the surface plane

$$-k\frac{\partial t}{\partial x} = \pm h(t_s - t_0) \tag{87}$$

For the infinite slab, the differential equation (20) is unchanged, but the boundary conditions (23) and (24) become

$$k\frac{\partial t}{\partial x} = h(t_s - t_0) \qquad \text{at} \qquad x = 0 \tag{88}$$

and

$$k\frac{\partial t}{\partial x} = -h(t_s - t_0) \qquad \text{at} \qquad x = 2R \tag{89}$$

As a result, the solution is more complicated than that outlined above for the case of $h = \infty$.

The four cases of semi-infinite solid, infinite slab, infinite cylinder, and sphere have been worked out for the case of finite surface coefficients and for initially constant temperature distributions. The resulting equations are found to represent the relations between the groups $\Delta\left(= \frac{t - t_0}{t_1 - t_0}\right)$, $\tau\left(= \frac{\alpha\theta}{R^2} = \frac{k\theta}{\rho C R^2}\right)$, k/hR, and r/R, all of which are dimensionless ratios. This fact was noted by Gurney and Lurie,* who prepared charts relating these four quantities for each solid shape. These charts, reproduced by Perry,† together with Newman's rule for combining shapes (which also holds when h is finite) provide a basis for approximate calculation in most cases met in practice.

The resultant temperature at any point in a body due to the action of several simultaneously imposed conditions over a time θ may be determined by a simple principle of summation, which owes its validity to the fact that the basic differential equation

* *Ind. Eng. Chem.*, **15**, 1170 (1923).

† "Chemical Engineers' Handbook," McGraw-Hill Book Company, Inc., New York, p. 840.

for conduction heat transfer is linear.* As an example of this method, consider a body with known initial temperature distribution exchanging heat with its surroundings at t_s and simultaneously receiving heat at a specified rate from some source in its interior. After any time θ, the temperature at any point may be obtained by adding (1) the temperature that would be obtained if the surface were maintained at zero and there were no heat received from the interior source; (2) the temperature that would be obtained if the solid initially at zero throughout be heated by having its surface maintained at t_s for time θ, there being no heat reception from the interior source during this process; and (3) the temperature that would be obtained if the solid initially at zero throughout were to receive heat at the specified rate from the interior source for time θ, the surface being maintained at zero throughout this process.

The extension of the summation principle to two or more effects following each other is quite simple. As a specific example, assume an infinite slab at a uniform temperature t_0 to be heated by having its faces held at t_1 for a time θ_1; the temperature of the faces is then changed to t_2 and held constant for an additional time θ_2. Referring to the Eq. (41) for a slab with negligible surface resistance to heat transfer, let Δ_3 be the calculated value for $\tau = \tau_1 + \tau_2 = \alpha(\theta_1 + \theta_2)/R^2$ and Δ_2 be the calculated value for $\tau_2 = \alpha\theta_2/R^2$. The value of the resulting temperature at any x is

$$t = t_0 + (t_1 - t_0)(1 - \Delta_3) + (t_2 - t_1)(1 - \Delta_2) \tag{90}$$

or

$$t - t_2 = (t_0 - t_1)\Delta_3 + (t_1 - t_2)\Delta_2 \tag{91}$$

This may be shown for the case of a solid slab by combining (41) and (46). In the second period θ_2, the face temperature is t_2, and at the start of this period the temperature elevation above t_2, represented by $f(x')$, is

$$f(x') = (t_0 - t_1)\Delta_1 + (t_1 - t_2) \tag{92}$$

where Δ_1 is given by (41) for $\tau = \tau_1$. If this series is substituted for $f(x')$ in (47) and the integration performed in each term, the desired result is obtained. For example, in the first term

* See NESSI and NISSOLE, "Methode graphiques pour l'etude des installations de chauffage," Dunod, Paris, 1929.

$$\int_0^{2R} f(x') \sin \frac{\pi x'}{2R} dx' = \frac{4R}{\pi}(t_0 - t_1)e^{-\left(\frac{\pi}{2}\right)^2 \tau_1} + \frac{4R}{\pi}(t_1 - t_2)$$

and the final result is

$$\gamma = t - t_2 = \frac{4}{\pi}(t_0 - t_1)\left[e^{-\left(\frac{\pi}{2}\right)^2 (\tau_1 + \tau_2)} \sin \frac{\pi x}{2R} + \frac{1}{3} e^{-9\left(\frac{\pi}{2}\right)^2 (\tau_1 + \tau_2)} \sin \frac{3\pi x}{2R} + \cdots \right] + \frac{4}{\pi}(t_1 - t_2)\left[e^{-\left(\frac{\pi}{2}\right)^2 \tau_2} \sin \frac{\pi x}{2R} + \frac{1}{3} e^{-9\left(\frac{\pi}{2}\right)^2 \tau_2} \sin \frac{3\pi x}{2R} + \cdots \right] = (t_0 - t_1)\Delta_3 + (t_1 - t_2)\Delta_2 \quad (93)$$

By an extension of this procedure, it may be shown that if the surface temperature of the slab initially at t_0 throughout is maintained at t_1, t_2 . . . t_n for times of θ_1, θ_2 . . . θ_n, respectively, the final temperature t at any point will be given by the equation

$$(t - t_n) = (t_0 - t_1)\Delta_{\tau_1 + \tau_2 + \tau_3 + \cdots \tau_n} + (t_1 - t_2)\Delta_{\tau_2 + \tau_3 + \cdots \tau_n} + \cdots (t_{n-1} - t_n)\Delta_{\tau_n} \quad (94)$$

where $\Delta_{\tau_1 + \tau_2 + \cdots \tau_n}$ denotes Δ calculated from (41) for

$$\tau_1 + \tau_2 + \cdots \tau_n = \frac{\alpha(\theta_1 + \theta_2 + \cdots \theta_n)}{R^2}$$

When the surface temperature is a continuous function of the time θ, varying from t_1 to t_n during the time $\theta = 0$ to $\theta = \theta$, there is an infinite number of terms in (94), and the summation may be replaced by an integration to give

$$t - t_n = \int_{t_s = t_1}^{t_s = t_n} \Delta \, dt_s \quad (95)$$

where t_s is the surface temperature at time θ. Given the functional relation between t_s and θ, this integral may be evaluated graphically as the area under a curve of Δ, calculated from (41), vs. t_s. This treatment is also valid for other shapes and for a constant finite value of the surface coefficient, in which case Δ may be evaluated from the appropriate Gurney-Lurie chart.

It is possible to allow for variation in the surface coefficient h by taking a fictitious surrounding temperature such that this temperature, taken together with the original h, predicts the actual rate of surface heat transfer. Thus if h_0 is the initial coefficient and h is the coefficient at time θ when actual surface

temperature is t_s, the fictitious surface temperature t_s' for use in the preceding equations is calculated from the equation

$$(t_s' - t_a)h_0 = (t_s - t_a)h \tag{96}$$

where t_a is the temperature of the surroundings.

105. Steady-state Heat Conduction. The simpler problems in heat conduction in the steady state are frequently encountered in practice, and the equations applicable are well known. In principle, these simpler problems are all special cases of the solution of (16). Occasional problems require the use of the methods illustrated above, and the solutions for some problems in steady-state heat conduction through furnace walls of irregular shapes may be exceedingly difficult to obtain.

As an example of the general method, consider the steady-state heat conduction in a square plate in which one edge has a temperature t_1 and the other three edges are maintained at a constant temperature t_0. The square has a side of length R. Once the steady state is reached, $\partial t/\partial\theta = 0$, and (16) becomes

$$\frac{\partial^2 t}{\partial x^2} = -\frac{\partial^2 t}{\partial y^2} \tag{97}$$

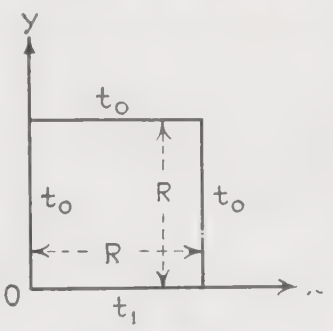

FIG. 56.

Following the same procedure as in the example of the infinite slab, we let $\Delta = (t - t_0)/(t_1 - t_0)$ and assume a solution of the form

$$\Delta = Y \cdot X$$

where Y is independent of x, and X is independent of y. This enables the variables to be separated and gives the two ordinary differential equations

$$\frac{1}{X}\frac{d^2X}{dx^2} = -\frac{1}{Y}\frac{d^2Y}{dy^2} = -a^2$$

where a is an arbitrary constant. Solving separately and replacing in $\Delta = Y \cdot X$, we have

$$\Delta = (Ae^{ay} + Be^{-ay})(C \sin ax + D \cos ax) \tag{98}$$

The boundary conditions are (see Fig. 56)

$$\Delta = 0 \quad \text{at} \quad x = 0 \tag{99}$$

$$\Delta = 0 \quad \text{at} \quad x = R \tag{100}$$

$$\Delta = 1 \qquad \text{at} \qquad y = 0 \tag{101}$$

$$\Delta = 0 \qquad \text{at} \qquad y = R \tag{102}$$

From (99), it follows that there can be no cosine term, and $D = 0$. From (100), $\sin aR = 0$, whence $aR = n\pi$, and $a = n\pi/R$. By the last condition,

$$Ae^{n\pi} + Be^{-n\pi} = 0$$

whence

$$A = -Be^{-2n\pi}$$

To obtain a general solution, we add an infinite number of the solutions (98) for all positive values of the integer n. Placing $B_nC_n = B_n'$ this leads to the result

$$\Delta = \sum_{n=1}^{n=\infty} B_n'(e^{-\frac{n\pi y}{R}} - e^{n\pi\left(\frac{y}{R}-2\right)}) \sin \frac{n\pi x}{R} \tag{103}$$

Substituting $\Delta = 1$ at $y = 0$ gives

$$1 = \sum_{n=1}^{n=\infty} B_n'(1 - e^{-2n\pi}) \sin \frac{n\pi x}{R} \tag{104}$$

B_n' is evaluated by comparing this with the sine series (40) for unity, and it follows that

$$B_n' = \frac{2}{n\pi} \frac{[1 - (-1)^n]}{(1 - e^{-2n\pi})} \tag{105}$$

The solution is thus obtained as

$$\Delta = \frac{4}{\pi}\left(\frac{e^{\pi\left(\frac{y}{R}-2\right)} - e^{-\frac{\pi y}{R}}}{e^{-2\pi} - 1} \sin \frac{\pi x}{R} + \frac{1}{3}\frac{e^{3\pi\left(\frac{y}{R}-2\right)} - e^{-\frac{3\pi y}{R}}}{e^{-6\pi} - 1} \sin \frac{3\pi x}{R} + \cdots\right) \tag{106}$$

If this is differentiated with respect to y, the temperature gradient in the y direction is obtained; and when $y = 0$ is substituted and integrated with respect to x, the rate of heat loss q from the hot edge is found as

$$q = -k(t_1 - t_0)\int^R \left(\frac{\partial \Delta}{\partial y}\right)_{y=0} dx \tag{107}$$

A graphical method for estimation of steady-state heat conduction in irregular shapes has been described by Awberry and Schofield.* This may sometimes be used advantageously to estimate heat loss through special shapes, as at the right-angle junction of two thick furnace walls.

106. Graphical Solutions of Problems in Unsteady-state Diffusion and Heat Conduction. Many of the practical problems of unsteady-state diffusion and heat conduction may be solved graphically by the method of Schmidt.† This ingenious procedure enables one to obtain approximate numerical solutions of problems that would be exceedingly difficult, if not impossible, to treat analytically and may be employed successfully without a knowledge of the formal methods of solving partial differential equations.

Consider the conduction equation for an infinite slab

$$\frac{\partial t}{\partial \theta} = \alpha \frac{\partial^2 t}{\partial x^2} \tag{20}$$

where t represents the temperature at any point, θ time, x the distance from one face, and α the diffusivity $k/C\rho$. Let $\Delta\theta$ represent a small but finite increment of time and Δx represent a small but finite increment of x. Since temperature varies with both time and distance x, let $\Delta_\theta t$ represent a small increment of t due to the change $\Delta\theta$ in time for a constant value of x, and let $\Delta_x t$ represent a corresponding increment of t due to the change Δx in x for a constant value of θ. Then $\partial t / \partial\theta$ is written $\Delta_\theta t / \Delta\theta$, and $\partial t / \partial x$ is written $\Delta_x t / \Delta x$. Let $\Delta_x^2 t$ represent the difference between two successive values of $\Delta_x t$ caused by a change Δx in x. Then Eq. (20) may be written

$$\frac{\Delta_\theta t}{\Delta\theta} = \alpha \frac{\Delta_x^2 t}{(\Delta x)^2} \tag{108}$$

or

$$\Delta_\theta t = \alpha \frac{\Delta\theta}{(\Delta x)^2} \Delta_x^2 t \tag{109}$$

In Fig. 57, temperature is plotted as ordinate vs. x as abscissa.

* *Proc. 5th Internat. Congress Refrig.*, **3**, 591 (1929).

† "Foeppls Festschrift," Julius Springer, Berlin, 1924, p. 179; see also Nessi and Nissole.

with increments of x indicated by the vertical parallel lines separated by a distance Δx. Let $t_{n,m}$ refer to the temperature at a position $n\Delta x$ from the origin after $m\Delta\theta$ units of time. The upper curve represents the temperature distribution at any instant $m\Delta\theta$, as indicated by the temperatures marked on the figure. Using the system of subscripts as defined, we write

$$\begin{aligned}\Delta_\theta t &= t_{n,m+1} - t_{n,m}\\ \Delta_x t &= t_{n+1,m} - t_{n,m}\\ \Delta_x^2 t &= \Delta_x(\Delta_x t) = (t_{n+1,m} - t_{n,m}) - (t_{n,m} - t_{n-1,m})\end{aligned} \tag{110}$$

Substituting these values in (109), we have

$$t_{n\,m+1} - t_{n,m} = \alpha\frac{\Delta\theta}{(\Delta x)^2}[(t_{n+1,m} - t_{n,m}) - (t_{n,m} - t_{n-1,m})] \tag{111}$$

In constructing a plot such as Fig. 57 for the solution of any actual problem, we are at liberty to choose Δx and $\Delta\theta$ of any size we please. Let these be chosen to make

$$\alpha\frac{\Delta\theta}{(\Delta x)^2} = \frac{1}{2} \tag{112}$$

Equation (111) then reduces to

$$t_{n,m+1} - t_{n,m} = \tfrac{1}{2}[t_{n+1,m} - 2t_{n,m} + t_{n-1,m}]$$

or

$$t_{n,m+1} = \tfrac{1}{2}(t_{n+1,m} + t_{n-1,m}) \tag{113}$$

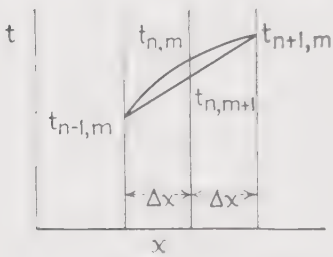

FIG. 57.—Basis of Schmidt method.

This relation is the basis of the Schmidt method. It states that the temperature at any point at any time is the arithmetic mean of the two temperatures Δx away on either side at a time $\Delta\theta$ previously. Thus in Fig. 57, the new temperature at the middle point, after an increment of time $\Delta\theta$, is the arithmetic mean of the previous values Δx at each side. It is clear that it may be obtained graphically by drawing a straight line through the points representing the two previous temperatures at $(n - 1)\Delta x$ and at $(n + 1)\Delta x$. The meaning of this basic rule must be kept clearly in mind in carrying out the graphical constructions for practical problems.

Figure 58 indicates diagrammatically how the method is applied to the cooling of an infinite solid slab initially at a uniform temperature t_i when both faces are suddenly cooled to t_0.

The slab is symmetrical about the central plane, so it is necessary to treat only one-half. The half-thickness R is divided into an integral number of increments Δx and vertical lines drawn to mark off these divisions. Although, in the example shown, only three divisions are made, it will be apparent that the accuracy of the method is improved by taking a larger number of divisions, *i.e.*, by making Δx small. When Δx is chosen (in this case R 3), it follows that the time interval $\Delta\theta$ is now fixed by (112).

The initial temperature of the slab is represented by the horizontal line kc. The temperature at the surface plane A is suddenly dropped to t_0, represented by point O. If the rule derived above is followed, the temperature $\Delta\theta$ later at plane B is the arithmetic mean of the original temperatures at planes A and C. This is located at b by the straight line Oa. The new value at plane C is the mean of p and c, which is again point a. The indicated temperature distribution at the time $\Delta\theta$ is the broken curve Oac. During the next time interval, the temperature at plane C falls to d as obtained by the straight line bc. In this time increment, the temperature at the central plane does not change, since it is convenient to visualize a point a' at a distance Δx past the center line where the temperature will always be the same as at plane C, and the new point e will be at the mean of a and a'. At the end of the third time increment, the temperature at B is f, located by the straight line Od. The temperature at the central plane is obtained by a horizontal line through d, because the point corresponding to d at the plane Δx past the center line is at the same ordinate as d.

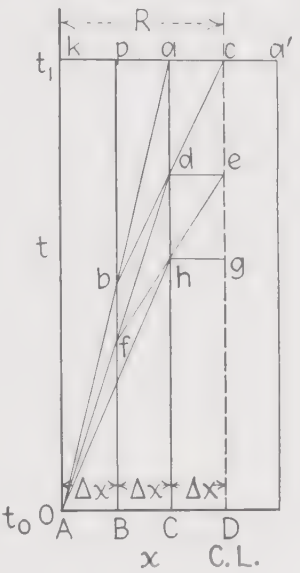

FIG. 58.—Construction near surface.

The process is continued, and it is evident that each lettered point represents the temperature at two or more successive values of $m\Delta\theta$. For example, on the central plane, point c represents the temperature at times 0, $\Delta\theta$, and $2\Delta\theta$; point e represents the temperature at times $3\Delta\theta$ and $4\Delta\theta$; point g, at $5\Delta\theta$ and $6\Delta\theta$, etc. The temperature at any time at any plane

is best obtained by drawing a smooth curve through the points on a plot of t vs. θ, $m\Delta\theta$ having been interpreted in terms of time through the known size of the $\Delta\theta$ increment [obtained by Eq. (112)].

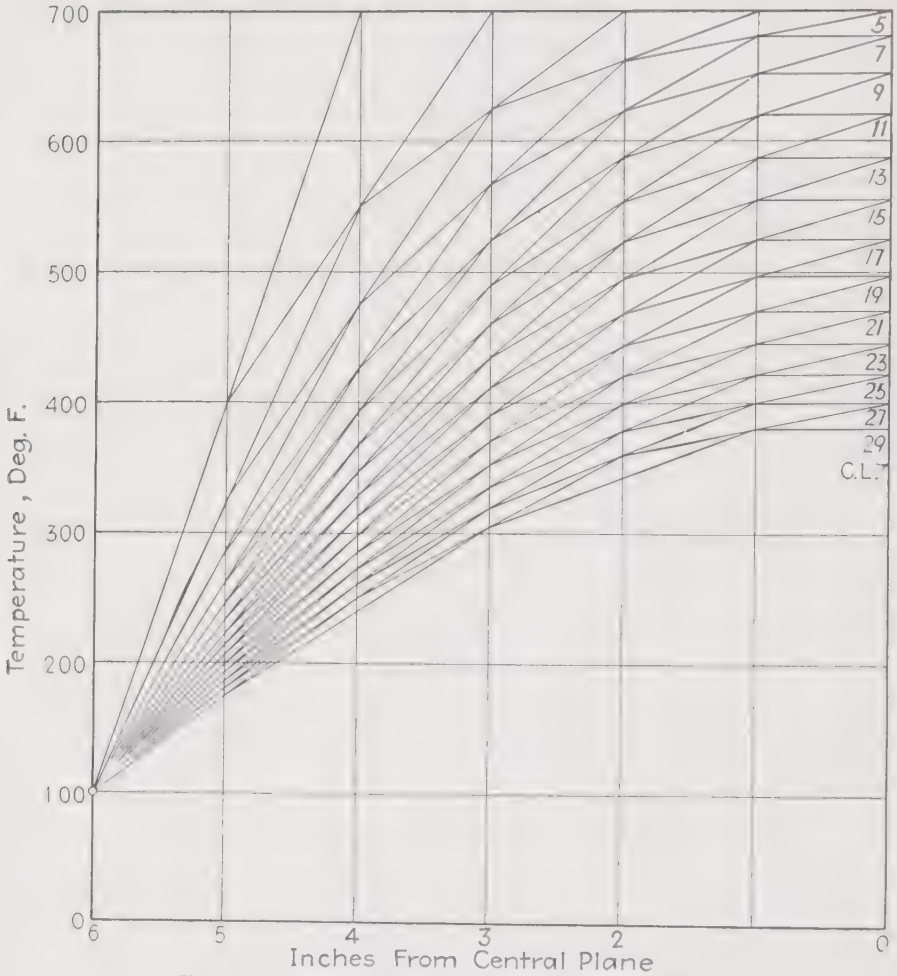

FIG. 59.—Construction for cooling of steel slab.

As a numerical example, consider the cooling of an infinite slab of steel 1 ft. thick, initially at a uniform temperature of 700°F., the faces of which are suddenly cooled and maintained at 100°F. Obtain the value of the temperature at the central plane after 15 min. The steel has a density of 490 lb. per cu. ft., a specific heat of 0.130, and a thermal conductivity of 25 B.t.u. (ft.)/(hr.)(sq. ft.)(°F.).

The increment Δx will be taken arbitrarily as 1 in., or 0.0833 ft. The thermal diffusivity α is calculated as

$$\alpha = \frac{k}{C\rho} = \frac{25}{0.13 \times 490} = 0.392$$

The corresponding value of $\Delta\theta$ is obtained by substituting in (112), so that

$$\Delta\theta = \frac{(0.0833)^2}{2 \times 0.392} = 0.00885 \text{ hr.} = 0.53 \text{ min.}$$

and it is necessary to carry on the graphical process for

$$\frac{15}{0.53} = 28.3 \text{ steps.}$$

The construction is shown on Fig. 59, which shows the points on the center line marked with the corresponding values of m

FIG. 60.—Center-line temperature vs. time for cooling of steel slab.

in order to keep track on the construction. Figure 60 shows the temperatures at the central plane plotted vs. θ. The temperature is 382°F. at 14.8 and at 15.4 min., and the desired value of the temperature at the center may therefore be taken as 382°F.

Figure 60 also shows a solid curve representing the series expansion as given by (41) for $x = R$. It may be noted that after 7 min. the curve passes regularly through the second of each pair of points, indicating that the values obtained for the odd values of m are the more reliable. At 15 min., the value calculated by the analytical method is approximately 384°F.

The accuracy obtainable by the graphical method is clearly dependent on the care taken in making the graphical construction and on the number of increments of x used. In the case illustrated by Fig. 60, it is apparent that the accuracy varies with time, being much better at large values of θ than near the start. A better result would be obtained if Δx were taken much smaller for the first few steps. After the center-line temperature had fallen appreciably, a change to a larger value of x could then be made. If this is done, it is important to note that $\Delta\theta$ changes also. The examples sketched have all assumed an initial temperature or concentration symmetrical about the center line. If the initial temperature is not symmetrical, the whole slab must be treated and the lines crossing the central plane will no longer be horizontal.

Various more or less arbitrary procedures may be followed in starting the construction. That followed in the example given above leads to serious errors in the temperature distribution near the beginning of the cooling process. This is evident, not only from Fig. 60, but by a comparison of the broken curves of Fig. 59 with the curves calculated from the series (41) shown on Fig. 54. Fishenden and Saunders* first draw in a curve calculated for a semi-infinite solid and then proceed with the graphical construction. This procedure is based on the reasoning that changes near the surface of a finite solid near the start of the cooling are essentially the same as though the solid were infinitely thick.

The solution of (20) for the case of the semi-infinite solid is

$$\Delta = \frac{2}{\sqrt{\pi}}\int_0^y e^{-v^2}dy \tag{114}$$

where $y = x\ 2\sqrt{\alpha\theta}$, and x represents the distance from the surface. The right-hand side is the so-called "probability integral," values of which are tabulated in mathematical tables. At the end of the first time increment,

$$\theta = \Delta\theta = \frac{1}{2}\frac{(\Delta x)^2}{\alpha} = \frac{x^2}{2\alpha n^2}$$

* "The Calculation of Heat Transmission," H. M. Stationery Office, London, 1932.

whence

$$y = \frac{x}{2\sqrt{\alpha\theta}} = \frac{n}{\sqrt{2}}$$

When n is 1, y is 0.707, and Δ is 0.683; when n is 2, y is 1.414, and Δ is 0.954. These points are placed on the figure, and lines connecting them represent the temperature distribution after one time increment. For example, in Fig. 61, point a is placed at an ordinate $0.683(t_1 - t_0)$ and d placed at the second plane at the ordinate $0.954(t_1 - t_0)$. The broken curve $Oadgp$ is then taken to represent the temperature distribution at $m = 1$.

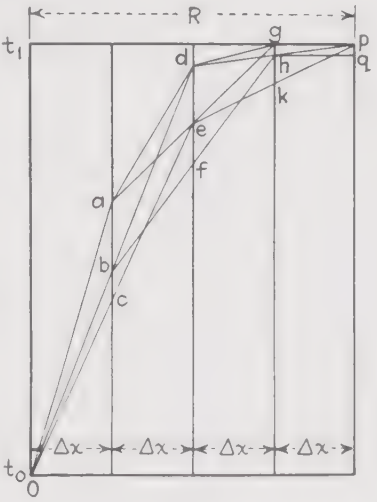

FIG. 61.

It may be noticed that in Fig. 58 the construction indicates a temperature change only every second time increment. Point b represents the temperature at plane B after one and after two time increments. The resulting time-temperature curve, such as Fig. 60, is made up of a large number of small steps. If the initial temperature distribution is not uniform, a new point may be obtained at each Δx for every time increment. If the method just described is employed, the subsequent construction may be made to show changes at each $\Delta\theta$. In Fig. 61, $Oadgp$ is the curve for $\Delta\theta = 1$. At $\Delta\theta = 2$, point b is obtained by joining Od, point c by joining ag, etc. Although this procedure is more tedious, the result is more accurate in detail than if alternate temperatures only are changed by each new construction. For large values of θ the two procedures give essentially the same result.

If the initial temperature distribution through the slab is not constant, the procedure is not changed. Figure 62 illustrates the construction for a slab of steel where the initial temperature distribution is given by the relation

$$t_1(°\text{F.}) = 500 + 7z^2$$

where z is the distance in *inches* from the *central plane*. Since the temperatures will be symmetrical about the center, only

one-half need be treated. The thickness and properties of the slab are taken as before, and 28.3 steps are required, with each $\Delta\theta$ representing 0.53 min. The temperature at the central plane after 15 min. is obtained as 307°F.

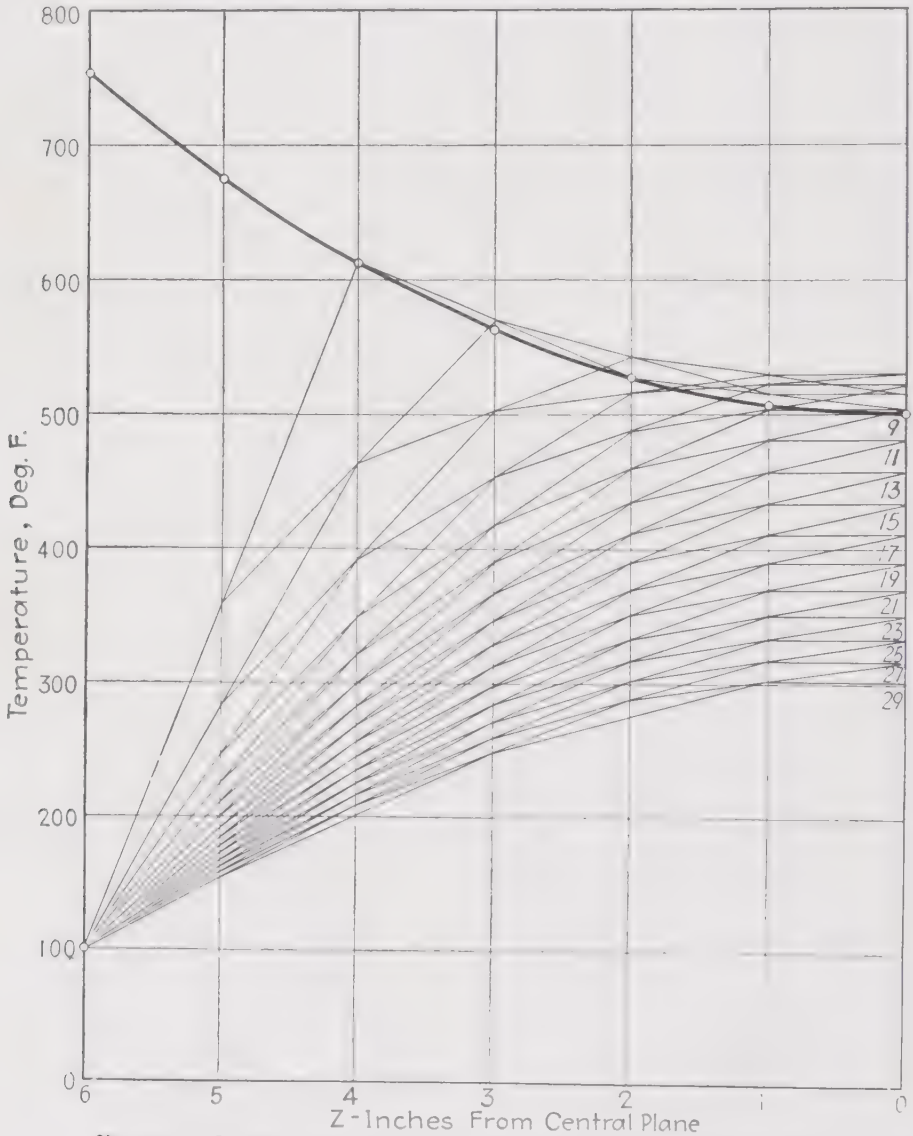

FIG. 62.—Cooling with initial parabolic temperature distribution.

This may be compared with the analytical result, obtained by substitution in (47). First, the initial temperature distribution is expressed in terms of γ and x', the distance in *feet* from *one face*, with the result

$$\gamma = 652 - 1008x' + 1008(x')^2 \qquad \text{at} \qquad \theta = 0$$

Here γ is defined as $t - 100$ (see Par. 100). Substituting this for $f(x')$, we have

$$\int_0^{2R} (652 - 1{,}008x' + 1{,}008(x')^2) \sin \frac{n\pi x'}{2R} dx' = \left[\frac{2{,}016}{n^3\pi^3} - \frac{652}{n\pi} \right](-1^n - 1)$$

This is substituted in (41), giving

$$\gamma = \frac{1}{R}(-1^n - 1) \sum_{n=1}^{n=\infty} \left(\frac{2{,}016}{n^3\pi^3} - \frac{652}{n\pi} \right) e^{-n^2\left(\frac{\pi}{2}\right)^2 \tau} \sin \frac{n\pi x}{2R} \qquad (115)$$

For the central plane of a slab 1 ft. thick at 15 min., $x = R$, $2R = 1$, $\tau = 0.392$, and this reduces to

$$\gamma = 4(54.3 - 0.011 + \cdots) = 217$$

The temperature is $100 + 217 = 317°$, which may be compared with the approximate value of 307° obtained by the graphical method.

As another example, consider the case of the interdiffusion of two gases in a cylinder, the analytical treatment of which is discussed in Par. 101. Assume that a partition in the center of a gas cylinder 125 cm. long separates equal quantities of helium and methane, each at 5 atm. total pressure. The partition is removed and the two gases allowed to mix. Assuming the mixing to take place by molecular diffusion only, calculate the time required for the average mol fraction methane to fall to 0.7 in one half and rise to 0.3 in the other half. The diffusion coefficient D may be taken as 0.131 sq. cm. per sec. The construction is shown in Fig. 63, where each half of the cylinder is divided into six increments of x, or $\Delta x = 10.42$ cm. It is apparent that the concentration of both gases at the central plane will instantly become 0.5 when the partition is removed; and the construction for each half is built on this point, which is analogous to the face temperature in the cooling of a slab. The construction is shown for both halves of the cylinder, although it will be apparent that the system is symmetrical about the center and but one half need be drawn.

At the end of the cylinder, no diffusion occurs and $\partial P/\partial x = 0$. This is the same condition as held for the infinite slab, where no heat crosses the center line. The construction is made just as though there were another cylinder at each end representing a mirror image of the first and alternate construction lines drawn horizontal at the end of the cylinder. By (112)

$$\Delta\theta = \frac{(\Delta x)^2}{2D} = \frac{10.42^2}{2 \times 0.131} = 414 \text{ sec.}$$

Since the average concentration of methane is to be 0.7 on one side, the construction is continued until the area under the curve

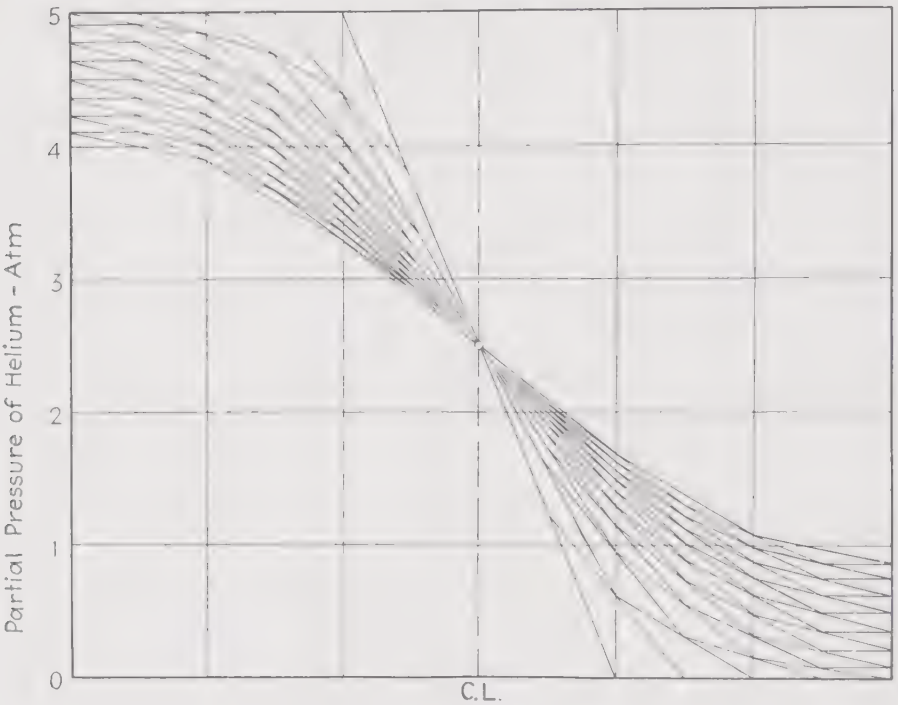

FIG. 63.—Interdiffusion of gases.

is 0.7 times the original area. This is found to occur after 20 steps, or

$$\frac{20 \times 414}{3{,}600} = 2.3 \text{ hr.}$$

This value checks almost exactly with that calculated from the analytical result (56).

The graphical method may also be employed in unsteady-state conduction or diffusion problems where the surface coeffi-

cient is finite. By a heat balance on the surface plane, we may write

$$k\left(\frac{\partial t}{\partial x}\right)_{x=0} = h(t_s - t_a) \tag{116}$$

where k is the thermal conductivity of the solid, t is the temperature of the solid at any point at a distance x from the surface, h is the surface coefficient of heat transfer, t_s is the temperature at the surface, and t_a is the temperature of the surrounding fluid medium. Figure 64 illustrates the construction for the cooling

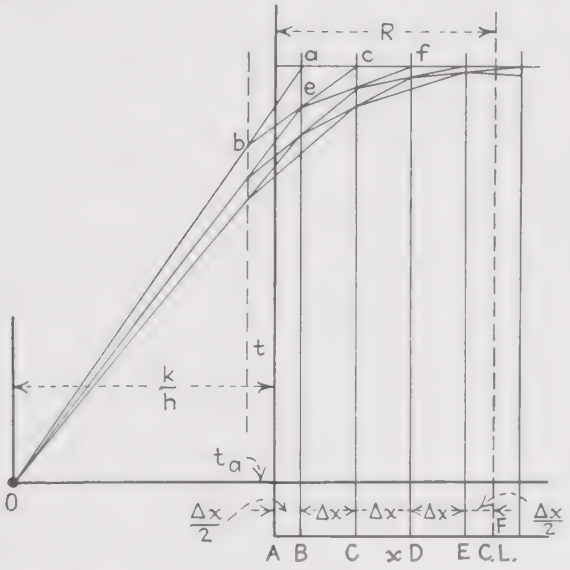

FIG. 64.—Construction allowing for finite surface resistance.

of an infinite slab. As before, the slab is divided into an arbitrary number of increments Δx, but this time they are spaced slightly differently, with the dividing lines drawn at $\frac{1}{2}\Delta x$, $\frac{3}{2}\Delta x$, etc. Rewriting (116) gives

$$\left(\frac{\partial t}{\partial x}\right)_{x=0} = \frac{(t_s - t_a)}{k/h} \tag{117}$$

from which it is apparent that the slope of the temperature curve at the boundary surface is equal to the ratio of the ordinate $(t_s - t_a)$ to a constant k/h. A construction point O is placed at the ordinate t_a and at a distance (k/h) from the surface (note that k/h has the dimensions of length), and the two vertical construction lines shown at $\Delta x/2$ out from the surface plane and

Δx 2 the other side of the central plane are drawn in. Any line drawn to point O from a point on the line representing the surface plane will have a slope $(t_s - t_a)$ $(k\ h)$, and so will cross the solid boundary with the correct slope as given by (117). The first step consists of the single line aO. The second step connects bc, and the third step places Oc and cf. Every other line drawn across the surface plane will thus have the correct slope as given by (117). The construction within the solid is the same as in the previous case. In drawing construction lines across the central plane, it is necessary to visualize only a set of lines representing a mirror image of those already placed on the half of the slab being studied and connect with the proper points on the line Δx 2 past the center line. In the case sketched, the construction lines crossing the center line will slope alternately up and down. The time corresponding to each $\Delta\theta$ or the number of steps needed for any given total time is obtained from (112), as before.

By the method just outlined, it is possible to obtain approximate numerical answers to problems that would be very difficult to solve analytically. For example, in the problem of the regenerator, the gas temperature varies regularly with time, and the coefficient h may be assumed to vary with the gas temperature. Thus both ordinate and abscissa of the point O of Fig. 64 undergo variation, but if the relation between these variables and time is known, a different construction point O may be used in each step, being located by the value of h and t_a for that instant.

Schmidt describes a way of treating a solid made up of different layers, the procedure being based on the fact that at the plane of contact the temperature gradients must be in inverse proportion to the thermal conductivities.

$$k_1\left(\frac{\partial t_1}{\partial x}\right) = k_2\left(\frac{\partial t_2}{\partial x}\right) \tag{118}$$

Since $\Delta\theta$ must be the same on both sides of the plane of contact, then from (112)

$$\alpha_1\frac{\Delta\theta}{(\Delta x_1)^2} = \alpha_2\frac{\Delta\theta}{(\Delta x_2)^2}$$

and

$$\frac{\Delta x_1}{\Delta x_2} = \sqrt{\frac{\alpha_1}{\alpha_2}} \tag{119}$$

Figure 65 indicates the construction near the plane of contact A-A. The points $abcdef$ are obtained by a construction appropriate to the problem, the new difficulty being how to connect c and d. Through d, draw the horizontal line shown dotted, locating a point g a distance $(\Delta x_2/2) \cdot (k_1/k_2)$ to the right of k. Connect cg, intersecting A-A at h, and connect hd. The broken line chd will then intersect the central plane with the proper

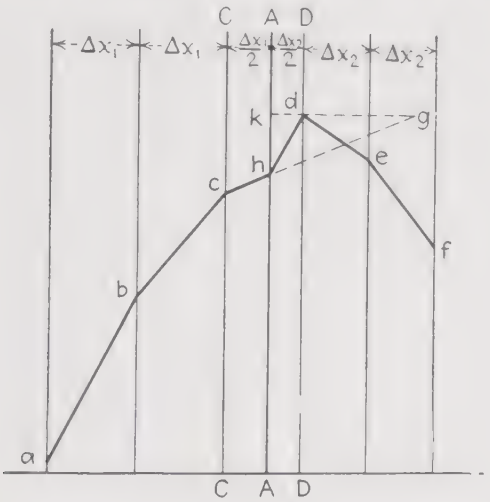

FIG. 65.—Dissimilar slabs in contact.

slopes, since from the geometry of the figure the distance hk is given by

$$hk = \left(\frac{\partial t_2}{\partial x_2}\right)\frac{\Delta x_2}{2} = \left(\frac{\partial t_1}{\partial x_1}\right)\frac{\Delta x_2}{2}\frac{k_1}{k_2}$$

so

$$k_2\left(\frac{\partial t_2}{\partial x_2}\right) = k_1\left(\frac{\partial t_1}{\partial x_1}\right)$$

and (118) is satisfied. To get a new point c' on plane C-C, connect b with a point on cg a distance $\Delta x_1/2$ to the right of A-A. To get a new point d' on D-D, connect e with a point on an extension of dh, $\Delta x_2/2$ to the left of A-A.

An alternative procedure for a composite slab is simpler and may frequently be used to advantage. To illustrate the method, we shall consider a slab made up of $6\frac{1}{2}$ in. of steel and 7 in. of bronze, in good thermal contact. The bronze has a thermal conductivity of 70 B.t.u. (ft.)/(hr.)(sq. ft.)(°F.) and a

diffusivity of 1.57 sq. ft. per hr. The steel has a conductivity of 25 and a diffusivity of 0.392. From (119),

$$\frac{\Delta x_B}{\Delta x_s} = \sqrt{\frac{1.57}{0.392}} = 2$$

We may choose Δx_B as 2 in. and Δx_s as 1 in., which will provide for one-half Δx on either side of the plane of contact and an even number through the rest of each solid. The time interval $\Delta\theta$ will be the same for both materials, 0.53 min. Now if two different linear abscissa scales are used for the two layers of the solid in plotting t vs. x, then a straight line drawn across the plane of contact can be made to have the correct slope in both materials. Referring to Fig. 66, it will be seen that the x scale is different for the steel than for the bronze. If the plot is drawn full scale for the steel, with Δx 1 in., then the 2-in. Δx of the bronze will be represented by

$$2 \times (\tfrac{3}{7}\tfrac{5}{0}) = 0.715 \text{ in.}$$

on the abscissa scale. Thus points b and f are connected by a straight line whose slope is numerically different on the two sides of A-A, the two values being in inverse ratio of the conductivities, as called for by (118). The auxiliary lines shown dotted are placed Δx_B 2 to the right of A-A and $\Delta x_s/2$ to the left of A-A. To locate a new point b, connect a with f; and to locate a new point d, connect e with k.

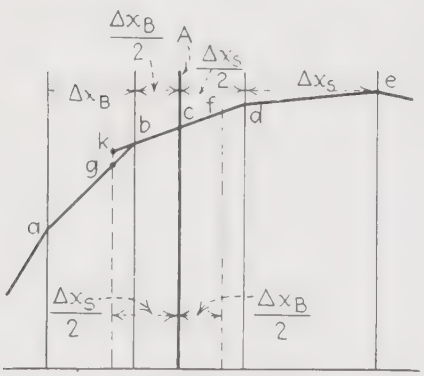

FIG. 66.

Various other problems may be treated by the graphical method described. Although it is limited in practical use to linear heat flow, Nessi and Nissole* describe the procedure to be followed in the general case of heat conduction in more than one direction. The same authors describe the use of a logarithmic abscissa scale for handling the case of heat conduction in a solid cylinder by the use of a plane diagram.

It should be possible to obtain an approximate result for the case of a solid in which the thermal diffusivity varies appreciably with temperature by allowing Δx to vary with t. The time

* *Loc. cit.*

increment $\Delta\theta$ is fixed by (112) as a function of Δx and the diffusivity α. Since the construction employs a plot of t vs. x, the width of the arbitrary Δx divisions may be made to vary with t so that $\Delta\theta$ will be constant. The diagram for a slab with parallel faces will then appear fan-shaped, the arbitrary Δx divisions being wider at the top (α increasing with temperature). The lines separating the divisions of the slab will in general be curved, although one division line in a central position may be chosen arbitrarily as straight and vertical. The problem of heat conduction with α dependent on temperature has been treated analytically by Sawada.*

* SAWADA, M., *J. Soc. Mech. Engs.* (*Japan*), **37**, No. 201, 15 (1934).

CHAPTER VII

NUMERICAL ANALYSIS

107. Empirical Equations. The representation of experimental data by means of algebraic equations is a practical necessity in engineering. Not only are such equations shorthand expressions for a large amount of data, but they serve as the necessary mathematical expressions by which the empirical information may be treated in subsequent mathematical operations. For the first use, the equation must be truly representative of the experimental data; for the second, it should be simple in form.

The form of the equation is frequently suggested by a theoretical analysis, and it is necessary only to evaluate certain constants. If the form is not known, dimensional analysis may be helpful in suggesting grouping of variables, and obvious practical considerations must not be overlooked. It is often evident that the curve must go through the origin or some fixed point, or perhaps become asymptotic to some definite value of one variable. The form of the empirical equation chosen must be consistent with such considerations.

108. Form of the Equation. The general problem of fitting data by an empirical equation may be divided into two parts: the determination of a suitable form of equation, and the evaluation of the constants. The determination of the form proceeds largely by trial, although certain rules may be laid down as practical aids. If the data can be plotted in such a way as to give a straight line, either by choice of graph paper or by a proper arrangement of variables for plotting, the linear form leads immediately to an expression relating the original variables. Likely forms are tested by plotting in such a manner as to make the expression linear, and the constants evaluated from the straight line obtained.

The experimental data may be assumed to be given in the form of a table of values of a variable y for corresponding values of

another variable x. For example, let it be desired to represent the following data by means of an empirical equation.

x	0.2	0.5	1.0	2.0	3.0	4.0
y	3.2	3.7	4.1	8.1	13.7	22.6

To make the problem general, it will be assumed that there is no additional information as to the nature of the function.

The data may always be represented exactly by a trigonometric series (see Chap. V) or by a polynomial having a sufficient number of terms; the six points tabulated may be represented by a polynomial of the fifth degree, containing six arbitrary con-

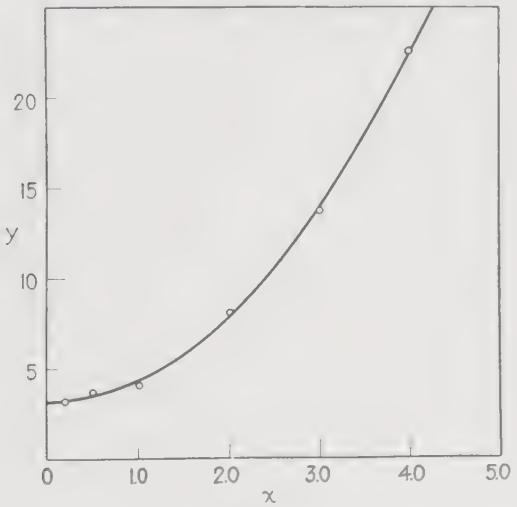

FIG. 67.

stants. This form is undesirable for three reasons: the constants would be quite difficult to evaluate; the expression obtained would be relatively complicated to use; and the determinations presumably involve experimental errors of such magnitude that an approximate representation is all that is justified. The problem, therefore, is to represent the data by an expression of the simplest possible form that fits the tabulated results within the estimated experimental error.

The first thing to do is to plot the data on ordinary rectangular coordinates, as shown in Fig. 67. This serves two purposes: The nature of the function is easily visualized so that the empirical form to be employed may be more readily selected; and the possibility of the simple linear form

$$y = a + bx \tag{1}$$

is tested at the outset. The points do not fall on a straight line on Fig. 67, and the simple linear form is not applicable. Usually, the next thing to do is to plot the data on logarithmic paper in order to test the form

$$y = ax^n \tag{2}$$

This form is very often applicable and is not too complicated for ordinary use. It is represented by a straight line of y vs. x on logarithmic paper, having a slope n and an "intercept" a at $x = 1$. If the ordinate and abscissa scales are equal, *i.e.*, if the distances along the axes are the same for a tenfold change in the variable y as for a tenfold change in x, the actual slope of the line is the value of n (Par. 127). If the scales are unequal, n is best obtained by substitution of coordinates of the straight line in (2). In the case of the illustrative example, it is apparent from Fig. 67 that (2) is not applicable, since the curve does not go through the origin. The power function (2) passes through the origin for all positive values of n; if n is negative, y decreases as x increases. The logarithmic plot may be omitted in this case.

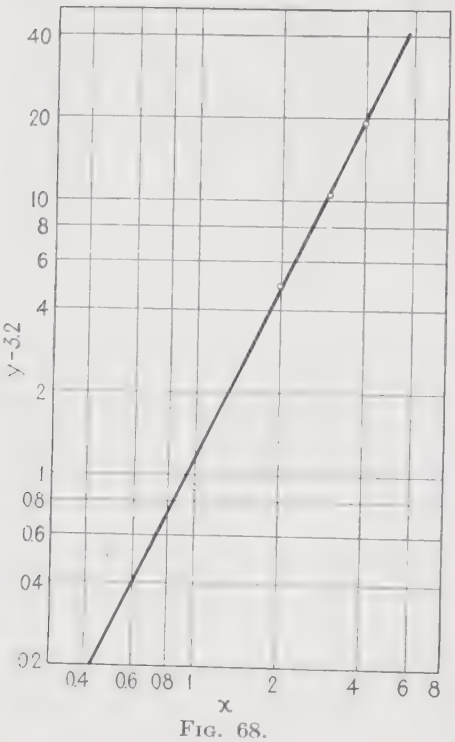

FIG. 68.

The *shape* of the curve is typical of expressions of the form (2), a fact which suggests that (2) might be applicable if a suitable change in coordinates were made. Since (2) must pass through the origin, the change must place the new origin at some point on the curve. An obvious possibility is the intercept $y = 3.2$ at $x = 0$. The new variables $y - 3.2$ and x are plotted in Fig. 68 and found to give a good straight line. The equation of the line is

$$y = 3.2 + ax^n \tag{3}$$

and may be assumed to be satisfactory provided that after evaluation of the constants the discrepancies between calculated and observed values are no greater than the assumed error in the experimental determinations. The procedures for evaluation of constants will be taken up in the next section.

The following is a useful summary of the simpler forms that may be used, with suggested methods of plotting to give straight lines.

(1) $y = a + bx$;	plot y vs. x
(2) $y = ax^n$;	plot log y vs. log x; or y vs. x on logarithmic coordinates
(3) $y = c + ax^n$;	first obtain c as intercept on plot of y vs. x, then plot log $(y - c)$ vs. log x; or y vs. x^n, or $(y - c)$ vs. x on logarithmic coordinates
(4) $y = ae^{bx}$;	plot log y vs. x; or y vs. x on semilogarithmic coordinates
(5) $y = ab^x$;	plot log y vs. x; or y vs. x on semilogarithmic coordinates
(6) $y = a + \frac{b}{x}$;	plot y vs. $\frac{1}{x}$
(7) $y = \frac{x}{a + bx}$;	plot $\frac{x}{y}$ vs. x
(8) $y = a + bx + cx^2$;	plot $\frac{y - y_n}{x - x_n}$ vs. x, where y_n, x_n are the coordinates of any point on a smooth curve through the experimental points
(9) $y = \frac{x}{a + bx} + c$;	plot $\frac{x - x_n}{y - y_n}$ vs. x, where y_n, x_n, are the coordinates of any point on the smooth curve

Various additional forms involving four constants are discussed by Lipka,* who gives a detailed treatment of the subject of selecting the form of the equation. Equations involving more than two constants should be not tested unless the simpler forms fail or unless it is obvious from the first graph that the function is quite complicated. Although type 3 appeared to be satisfactory in the case of the illustrative problem, it may be found that some other form, such as type 8, will fit the data better.

109. Determination of an Empirical Equation by Successive Approximation. Instead of attacking the problem of fitting the original data by an empirical equation, we may write any simple expression that approximates the function and then proceed

* "Graphical and Mechanical Computation," John Wiley & Sons, Inc., New York, 1921.

to the problem of fitting an empirical equation to the differences between the observed values and those computed by this simple expression. The data are plotted as y vs. x and the curve approximated by a function $f(x)$, which is preferably of some simple form such as $y = bx$, $y = a + bx$, or $y = ax^n$. An empirical equation for the differences $y - f(x)$, in terms of x, is then determined by the methods described in the preceding section. This procedure has the advantage that the errors involved in fitting the empirical equation apply to the differ-

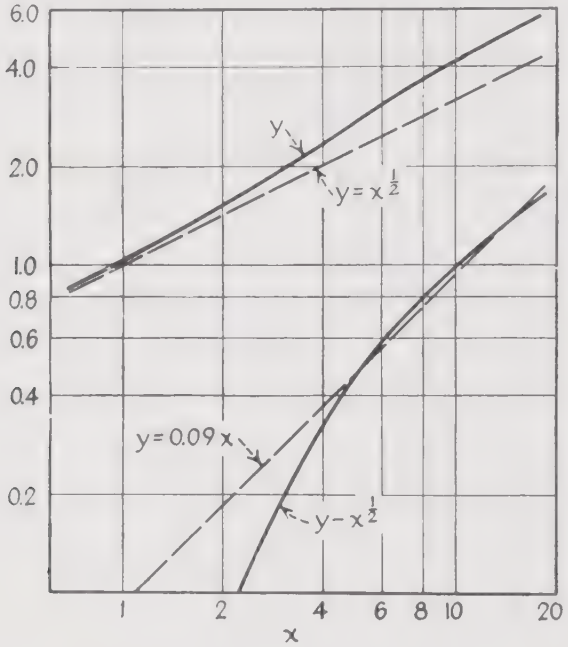

FIG. 69.

ences, which are small quantities if the first approximation is good. The function $f(x)$ should not only be of a simple form but should be so chosen that the differences will not pass through a maximum or minimum. It is obvious that the method may be extended by writing a second approximation for the first differences and then finding an empirical expression for the second differences.

Figure 69 represents a graph of y vs. x on logarithmic paper to be fitted by an empirical equation. This is first approximated by the dotted straight line representing the function $y = x^{\frac{1}{2}}$. The differences $y - x^{\frac{1}{2}}$ are plotted vs. x as shown by the lower solid curve. This is fitted approximately by the lower dotted

straight line, representing the function $y = 0.09x$. The original function is then expressed as

$$y = x^{\frac{1}{2}} + 0.09x$$

It is apparent from a comparison of the two lower curves that this expression fits the function within a maximum error of about 0.10 in y. A still better result may be obtained by writing an approximate expression for the first differences and then obtaining an empirical expression for the second differences. If this were done, the lower straight line $y = 0.09x$ would not be used, as this makes the second differences pass through a maximum. A straight line asymptotic to the upper end of the difference curve would be a better first approximation as the equation for the second difference would then be of a simpler form. In obtaining the empirical equation for the last differences plotted, the larger differences should be fitted closely, as these represent the larger errors in the function.

This method has obvious utility in engineering work because of its directness and simplicity, although some practice is needed if one is to avoid final difference functions that are difficult to fit empirically. The error in the final result may be made as small as desirable by continuing this process. By differentiation of the result, accurate values of the derivative may be obtained, and the method employed as an alternative procedure for numerical differentiation (see Par. 120).

110. Evaluation of Constants. The form of the empirical equation having been determined, the remaining problem is the determination of the arbitrary constants. This may be done (1) by writing the equation for the best straight line placed by visual inspection, (2) by the method of averages, and (3) by the method of least squares. The first method is often satisfactory in the practical cases encountered in chemical engineering, for the accuracy of the data seldom warrants the use of the more accurate but more complicated methods.

In the illustrative example given above, a straight line on logarithmic coordinates was obtained in Fig. 68. This passes through the points $y - 3.2 = 0.4$ at $x = 0.6$, and $y - 3.2 = 25$ at $x = 4.5$, whence

$$0.4 = a(0.6)^n$$

and

$$25 = a(4.5)^n$$

which give $a = 1.15$ and $n = 2.05$. Equation (3) becomes

$$y = 3.2 + 1.15x^{2.05} \tag{4}$$

This result may be tested by comparing the calculated and observed values of y for each value of x.

x	y	y_{calc}	R	R^2
0.2	3.2	3.2	0	0
0.5	3.7	3.5	−0.2	0.04
1	4.1	4.4	0.3	0.09
2	8.1	8.0	−0.1	0.01
3	13.7	14.1	0.4	0.16
4	22.6	22.9	0.3	0.09
			$\Sigma R = 0.7$	$\Sigma R^2 = 0.39$

The last two columns give the values of R and R^2, where R is the difference between the calculated and observed values of y. The maximum error is 0.4, and ΣR is 0.7. Even though the equation were a poor representation of the data, ΣR might be zero owing to cancellation of terms, and ΣR^2 is a better indication of how well the equation fits the data.

The method of averages involves the preliminary division of the data into groups corresponding in number to the number of the arbitrary constants to be evaluated. The constant 3.2 in (3) was obtained graphically as the intercept of the line of Fig. 67. Letting this be one of the constants to be evaluated, we have

$$y = c + ax^n \tag{5}$$

and the tabulated data will be divided into three groups to determine the three constants. Writing the six equations for R, we have

$$\left.\begin{aligned} R_1 &= c + a(0.2)^n - 3.2 \\ R_2 &= c + a(0.5)^n - 3.7 \end{aligned}\right\} \quad (a)$$

$$\left.\begin{aligned} R_3 &= c + a(1)^n - 4.1 \\ R_4 &= c + a(2)^n - 8.1 \end{aligned}\right\} \quad (b)$$

$$\left.\begin{aligned} R_5 &= c + a(3)^n - 13.7 \\ R_6 &= c + a(4)^n - 22.6 \end{aligned}\right\} \quad (c)$$

which are divided into three pairs. Setting $\Sigma R = 0$ in each group, we obtain the three equations

$$2c + \{(0.2)^n + (0.5)^n\}a - 6.9 = 0$$
$$2c + \{1 + (2)^n\}a - 12.2 = 0$$
$$2c + \{(3)^n + (4)^n\}a - 36.3 = 0$$

These may be solved simultaneously, giving $a = 1.07$, $c = 3.3$, and $n = 2.08$. When these values are used, ΣR is 0.2 and ΣR^2 is 0.22. It follows that the result

$$y = 3.3 + 1.07x^{2.08} \tag{6}$$

is somewhat better than (4). In general, the method of averages gives a better result than is obtained by placing the best straight line through the points on an ordinary sheet of graph paper, although the result is dependent on the method of grouping of the points. Consecutive grouping, as followed above, is usually the most reliable. If the number of points is not evenly divisible by the number of constants, the groups are necessarily unequal in size. If there had been eleven points, for example, groups (*a*), (*b*), and (*c*) might have contained four, three, and four equations, respectively.

111. Evaluation of Constants by Method of Least Squares. The principle of least squares states that the most probable value of a quantity obtainable from a number of measurements of equal precision is that value for which the sum of the squares of the errors is a minimum (see Par. 151). The error in a determination is the difference between the true value and the observed value of the quantity. The residual, denoted by R in the preceding paragraph, is the difference between the most probable and the observed value. The principle also applies when "residuals" are substituted for "errors" and is used in this form because the true value is not known. In using the principle, it is important to remember the basic assumption that the precision of each observation of the quantity is equal, which means that each value is subject to the same absolute accidental error. If the error in reading a scale is taken as some definite *length*, then the principle of least squares may be applied directly to numbers read from the scale only if the scale is *linear*. The necessary modification for other cases will be discussed below.

As extended to curve fitting, the principle of least squares states that the best curve (or empirical equation) is that for which the sum of the squares of the residuals is a minimum.

Again, it should be emphasized that equal precision is assumed for each observation. This assumption is valid not only if the errors involved are due to the uncertainty of reading a linear scale but also in a majority of cases where accidental error is introduced by faulty experimental technique. There are some cases where the accidental error introduces a variable precision, greater precision usually being obtained in the measurement of small values of the quantity.

As an example of the procedure, assume that it is desired to fit the data given in the preceding section by the empirical form

$$y = a + bx + cx^2 \tag{7}$$

The equations for the residuals are

$$\begin{aligned} R_1 &= a + bx_1 + cx_1^2 - y_1 \\ R_2 &= a + bx_2 + cx_2^2 - y_2 \\ R_3 &= a + bx_3 + cx_3^2 - y_3; \text{ etc.} \end{aligned}$$

Each equation is squared and the several equations added to give ΣR^2. The sum is differentiated with respect to each of the three constants and each result equated to zero, giving three conditions for which ΣR^2 is a minimum. The result is

$$\begin{aligned} \frac{\partial}{\partial a}(\Sigma R^2) &= 0 = 2(a + bx_1 + cx_1^2 - y_1) + \\ &\quad 2(a + bx_2 + cx_2^2 - y_2) + 2(a + bx_3 + cx_3^2 - y_3) + \cdots \qquad (8) \\ \frac{\partial}{\partial b}(\Sigma R^2) &= 0 = 2x_1(a + bx_1 + cx_1^2 - y_1) + \\ &\quad 2x_2(a + bx_2 + cx_2^2 - y_2) + 2x_3(a + bx_3 + cx_3^2 - y_3) + \cdots \\ \frac{\partial}{\partial c}(\Sigma R^2) &= 0 = 2x_1^2(a + bx_1 + cx_1^2 - y_1) + \\ &\quad 2x_2^2(a + bx_2 + cx_2^2 - y_2) + 2x_3^2(a + bx_3 + cx_3^2 - y_3) + \cdots \end{aligned}$$

which may be written

$$\left.\begin{aligned} na + b\Sigma x + c\Sigma x^2 - \Sigma y &= 0 \\ a\Sigma x + b\Sigma x^2 + c\Sigma x^3 - \Sigma xy &= 0 \\ a\Sigma x^2 + b\Sigma x^3 + c\Sigma x^4 - \Sigma x^2 y &= 0 \end{aligned}\right\} \tag{9}$$

where n is the number of observations.

For the numerical example the various products may be tabulated.

x	y	x^2	x^3	x^4	xy	x^2y
0.2	3.2	0.04	0.008	0.0016	0.64	0.128
0.5	3.7	0.25	0.125	0.0625	1.85	0.925
1	4.1	1	1	1	4.1	4.1
2	8.1	4	8	16	16.2	32.4
3	13.7	9	27	81	41.1	123.3
4	22.6	16	64	256	90.4	361.6
10.7	55.4	30.3	100.1	354.1	154.3	522.5

The three equations may be written

$$\begin{aligned} 6a + 10.7b + 30.3c - 55.4 &= 0 \\ 10.7a + 30.3b + 100.1c - 154.3 &= 0 \\ 30.3a + 100.1b + 354.1c - 522.5 &= 0 \end{aligned}$$

whence $a = 4.1$, $b = -1.37$, $c = 1.50$, and the equation is

$$y = 4.1 - 1.37x + 1.50x^2 \tag{10}$$

On calculating values of the residuals, it is found that $\Sigma R = 0.0$ and $\Sigma R^2 = 1.1$. The calculations have been carried out using a slide rule, and it is probable that the result might be improved. The solution of the three simultaneous equations involves moderately small differences, and it would be justifiable to carry more significant figures than are obtainable on a slide rule, even though the data are good to but one decimal place. Comparison of the values of ΣR^2 shows that the result does not represent the data as well as the form (6). This emphasizes the point that the method of least squares does not aid in selecting the best equation to fit the data.

If the equation is linear in the arbitrary constants, the procedure for determining these constants by the method of least squares follows the illustrative example just presented. If the equation is not linear in the constants, the function may be approximated by expansion into Taylor's series, all derivatives higher than the first being neglected. This procedure is explained in any standard text on least squares.*

The procedure may be simplified considerably if the values of one variable are equidistant, since a general solution of the

* See *e.g.*, D. P. Bartlett, "Method of Least Squares," Massachusetts Institute of Technology, 1900.

simultaneous equations may be obtained and the labor of subsequent solutions avoided. The equations for the constants in a fourth-degree polynomial have been obtained by Avakian* for the case of seven points. These are assumed to be spaced at equal intervals h, with the coordinates chosen so that $x = 0$ for the central point of the seven. The seven values of x, then, are $-3h$ $-$ $2h$, $-h$, 0, h, $2h$, and $3h$. It is desired to obtain the best value of the constants in the polynomial

$$y = a + bx + cx^2 + dx^3 + ex^4 \tag{11}$$

By the principle of least squares,

$$\Sigma R^2 = \Sigma(a + bx + cx^2 + dx^3 + ex^4 - y)^2 = \text{minimum}$$

If we differentiate with respect to each constant, and equate to zero, the conditions are obtained for which ΣR^2 should be a minimum. These are

$$\begin{aligned}
7a + b\Sigma x + c\Sigma x^2 + d\Sigma x^3 + e\Sigma x^4 - \Sigma y &= 0 \\
a\Sigma x + b\Sigma x^2 + c\Sigma x^3 + d\Sigma x^4 + e\Sigma x^5 - \Sigma xy &= 0 \\
a\Sigma x^2 + b\Sigma x^3 + c\Sigma x^4 + d\Sigma x^5 + e\Sigma x^6 - \Sigma x^2y &= 0 \\
a\Sigma x^3 + b\Sigma x^4 + c\Sigma x^5 + d\Sigma x^6 + e\Sigma x^7 - \Sigma x^3y &= 0 \\
a\Sigma x^4 + b\Sigma x^5 + c\Sigma x^6 + d\Sigma x^7 + e\Sigma x^8 - \Sigma x^4y &= 0
\end{aligned}$$

Let k represent the coefficient of h in the values of x. Then

$$\begin{aligned}
\Sigma x &= -3h - 2h - h + 0 + h + 2h + 3h \\
&= h\Sigma k = 0 = \Sigma x^3 = \Sigma x^5 = \Sigma x^7
\end{aligned}$$

Similarly, $\Sigma x^2 = h^2\Sigma k^2 = 28h^2$; $\Sigma x^4 = 196h^4$

$$\begin{aligned}
\Sigma x^6 &= 1{,}588h^6; & \Sigma x^8 &= 13{,}636h^8; \\
\Sigma xy &= h\Sigma ky; & \Sigma x^2y &= h^2\Sigma k^2y; \\
\Sigma x^3y &= h^3\Sigma k^3y; & \Sigma x^4y &= h^4\Sigma k^4y.
\end{aligned}$$

The five conditions may now be written

$$\begin{aligned}
7a + 28h^2c + 196h^4e - \Sigma y &= 0 \\
28h^2b + 196h^4d - h\Sigma ky &= 0 \\
28h^2a + 196h^4c + 1{,}588h^6e - h^2\Sigma k^2y &= 0 \\
196h^4b + 1{,}588h^6d - h^3\Sigma k^3y &= 0 \\
196h^4a + 1{,}588h^6c + 13{,}636h^8e - h^4\Sigma k^4y &= 0
\end{aligned}$$

* AVAKIAN, Thesis in the Department of Mathematics, Massachusetts Institute of Technology, 1933, done under the supervision of R. D. Douglass

Avakian gives the solution of these as

$$a = \tfrac{1}{9}\tfrac{1}{2}\tfrac{1}{4}(524\Sigma y - 245\Sigma k^2 y + 21\Sigma k^4 y) \tag{12}$$

$$b = \frac{397\Sigma ky}{1{,}512h} - \frac{7\Sigma k^3 y}{216h} \tag{13}$$

$$c = \frac{1}{3{,}168h^2}(-840\Sigma y + 679\Sigma k^2 y - 67\Sigma k^4 y) \tag{14}$$

$$d = \frac{1}{216h^3}(-7\Sigma ky + \Sigma k^3 y) \tag{15}$$

$$e = \frac{1}{3{,}168h^4}(72\Sigma y - 67\Sigma k^2 y + 7\Sigma k^4 y) \tag{16}$$

As a simple example of the use of this form, we may take the relation

y	2	3	2	−1	−2	−2	−1
x	0	1.5	3	4.5	6	7.5	9

We first move the origin along the x axis to the middle point and proceed to obtain an equation in terms of x', where

$$x = x' + 4.5.$$

The following table is prepared as an aid in substitution in the equations for the constants:

x'	y	k	ky	k^2y	k^3y	k^4y
−4.5	2	−3	− 6	18	− 54	162
−3.0	3	−2	− 6	12	− 24	48
−1.5	2	−1	− 2	2	− 2	2
0	−1	0	0	0	0	0
1.5	−2	1	− 2	− 2	− 2	− 2
3.0	−2	2	− 4	− 8	− 16	− 32
4.5	−1	3	− 3	− 9	− 27	− 81
	1		−23	13	−125	97

Substituting in (12), (13), (14), (15), and (16) gives

$$a = \tfrac{1}{9}\tfrac{1}{2}\tfrac{1}{4}[524(1) - 245 \times 13 + 21 \times 97]$$

$$b = -\frac{397 \times 23}{1{,}512 \times 1.5} + \frac{7 \times 125}{216 \times 1.5}; \text{ etc.}$$

whence $a = -0.68$; $b = -1.32$; $c = 0.21$; $d = 0.049$;

$$e = -0.0075;$$

and $y = -0.68 - 1.32x' + 0.21(x')^2 + 0.049(x')^3 - 0.0075(x')^4$ which may be converted to an equation in x, if desired, by substituting $x' = x - 4.5$. The calculation of the several values of y gives $\Sigma R = 0.02$ and $\Sigma R^2 = 0.36$. The nature of the function and the general agreement of the equation with the points are evident from Fig. 70.

Although the use of Eqs. (12) to (16) for the evaluation of the constants in a fourth-degree polynomial is limited to cases where points at seven equidistant values of x are given, the method has other uses to be discussed in a later section.

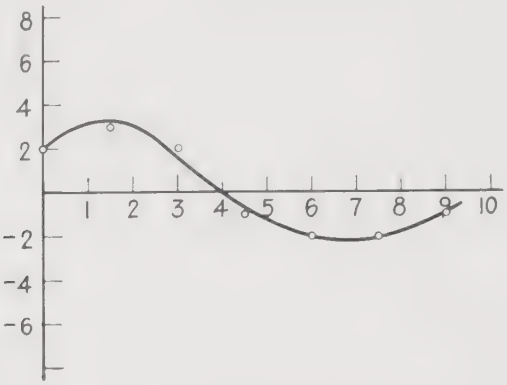

FIG. 70.

112. Least Squares with Determinations of Unequal Weight. It was emphasized in the preceding paragraph that the principle of least squares involves the assumption of equal precision for all determinations treated. This is valid in many cases, such as in any determination in which the precision depends on reading a linear scale, but there are many cases where the errors are more nearly constant percentage errors. Suppose, for example, that the rate of heat transfer in a steam-heated evaporator is being determined by measuring the condensate as it collects in a drum. The time to fill the drum is determined by an accurate stop watch, the principal error being one of $\pm\frac{1}{4}$ in. in reading the level in the drum. If the drum is filled to the same mark each time, then the constant absolute error in the level results in a constant percentage error in the variable time. The calculated heat-transfer coefficients are subject to a resulting constant percentage error from this source alone.

The best straight line through points on logarithmic paper as placed by visual inspection will tend to fall so that the linear

distances of the points from the line will be the least. Since distances represent differences of logarithms, the line will tend to be that for minimum percentage error. If there are two points at ordinates 30 and 50 at the same abscissa, the eye will tend to place the line just half-way between, at ordinate 38.7.

In fitting data by the equation

$$y = ax^n$$

the principle of least squares may be applied to the residuals

$$R = ax^n - y$$

although the procedure in evaluating a and n so that ΣR^2 is a minimum would be relatively complicated. This would be correct, however, on the assumption that y is subject to a constant absolute accidental error. As an alternative, we may treat the residuals

$$R = \log a + n \log x - \log y$$

but this would be correct only for a constant absolute accidental error in $\log y$, *i.e.*, for a constant *percentage* error in y.

The general method for finding the proper form of an empirical equation involves first finding some method of plotting the data so as to obtain a straight line. If the variables are x and y, then the straight line obtained is

$$y' = a + bx'$$

where x' and y' are both functions of x and y. The constants a and b having been obtained, the functions x' and y' are written in terms of x and y, and the desired empirical equation in x and y is obtained. If the method of least squares is applied in the ordinary way to determine a and b, then the values of the function y' are presumably subject to a constant absolute experimental error, as the residuals are

$$R = a + bx' - y' \tag{17}$$

In order to take care of the more usual case where the original determination of y is subject to a constant percentage experimental error, the method is modified by weighting the residuals (17). The procedure, described by Scarborough,* is based on the more general statement of the principle (see Par. 152) as follows:

* "Numerical Mathematical Analysis," The Johns Hopkins Press, Baltimore, 1930.

The best value of an unknown quantity obtainable from a number of determinations of unequal precision is that for which the sum of the weighted squares of the residuals is a minimum. The square of each residual is multiplied by its weight W and the equation obtained for which the sum of these products is a minimum. The weight W is defined as the number of observations of unit weight to which the single observation is equivalent. It may be shown that if a series of determinations of y subject to a constant percentage error is to be fitted by an empirical equation $y = f(x)$, the squares of residuals $R^2 = [f(x) - y]^2$ should be weighted by multiplying each squared term by a number that is proportional to $1/y^2$.

By proper weighting of residuals, it is possible to do two things: (1) allow for unequal precision in the determinations of the original variable y, and (2) weight the values of the function y' to correspond to any specified precision, equal or unequal, in the determination of y. Although the procedure in some cases is not particularly complicated, it is seldom justified in the treatment of chemical engineering data. After comparing the results obtained in several cases with and without weighting, Scarborough expresses the opinion that it is ordinarily not worthwhile to bother about the weights of the residuals.

If the determinations of both x and y are subject to errors of the same order of magnitude, we may fit the best line through the points by the method of least squares provided that a straight line is satisfactory. The procedure is given by Scarborough for the case where the residuals of both x and y are of equal weight. In practice, one variable is usually subject to much less error than the other and may be assumed to have been determined accurately, so that the procedure as outlined above may be followed.

The method of least squares has the practical disadvantage of requiring very accurate computation if the residuals of the empirical constants are to be determined with high precision. The residuals are small differences of relatively large numbers, and these numbers must be computed to a fairly large number of significant figures in order that the empirical constants will be sufficiently accurate. This is particularly true in the case of accurate data, which can be represented very precisely by an empirical equation.

113. Numerical Integration. Simpson's Rule. It is frequently necessary to obtain an approximate numerical value of a definite integral, and any one of several fairly rapid numerical methods may be employed instead of a graphical integration. If the area to be measured is visualized, it is usually apparent how it may be divided into a number of narrow trapezoids, the area of each approximated numerically, and the summation obtained. This was done on page 3 when the time required for the car to travel 300 miles was approximated by adding the approximate times for each of three 100-mile intervals. If the base of the figure (Fig. 71), having a length $x_3 - x_1$, is divided into n equal increments, and the $(n + 1)$ corresponding ordinates are $y_0, y_1 \ldots y_n$, then the area is given by

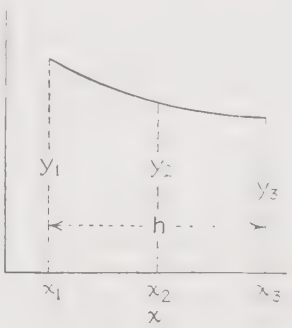

FIG. 71.

$$\int_{x_1}^{x_3} y\,dx = \frac{x_3 - x_1}{n}\left(\frac{y_0}{2} + y_1 + y_2 + \cdots y_{n-1} + \frac{y_n}{2}\right) \quad (18)$$

This method of finding the integral is known as the "trapezoidal rule."

A somewhat better method, much used by engineers, is Simpson's rule. Referring to Fig. 71, assume that the curve between x_1 and x_3 may be represented exactly by a cubic* or simpler equation, *i.e.*, assume

$$y = a_0 + a_1x + a_2x^2 + a_3x^3 \quad (19)$$

Referring to Fig. 71, y_1 is the value of the function at $x = x_1$, and y_3 is the value of the function at $x = x_1 + h$, where h represents the interval $x_3 - x_1$. By direct integration,

$$\int_{x_1}^{x_3} y\,dx = a_0h + \frac{a_1}{2}(2x_1h + h^2) + \frac{a_2}{3}(3x_1^2h + 3x_1h^2 + h^3) + \frac{a_3}{4}(4x_1^3h + 6x_1^2h^2 + 4x_1h^3 + h^4) \quad (20)$$

* It is frequently stated that Simpson's rule amounts to replacing the actual curve by a second-degree parabola over the interval x, $x + h$. As a matter of fact, it can be shown that the area under such a parabola passing through three equidistant points on any third-degree curve is the same as the area under the third-degree curve itself. Although it is true that the curve is replaced by the arc of a second-degree parabola for the interval involved, the integral obtained is actually accurate if the curve is a cubic.

By direct substitution in (19), y_1, y_2, and y_3 are obtained as follows:

$$y_1 = a_0 + a_1x_1 + a_2x_1^2 + a_3x_1^3$$
$$y_2 = a_0 + a_1\left(x_1 + \frac{h}{2}\right) + a_2\left(x_1 + \frac{h}{2}\right)^2 + a_3\left(x_1 + \frac{h}{2}\right)^3$$
$$y_3 = a_0 + a_1(x_1 + h) + a_2(x_1 + h)^2 + a_3(x_1 + h)^3$$

where x_2 is placed midway between x_1 and x_3, *i.e.*, at

$$x = x_1 + \left(\frac{h}{2}\right)$$

and y_2 is defined as the ordinate at that point. If the expressions for the values of y_1, y_2, and y_3 are expanded and compared with (20), it may be readily shown that

$$\int_{x_1}^{x_3} y\,dx = \int_{x_1}^{x_1+h} y\,dx = \frac{h}{6}(y_1 + 4y_2 + y_3) \qquad (21)$$

This is Simpson's rule.

The procedure in carrying out an actual integration is to note the ordinates (or values of the function) at the two limits and at a point midway between. The sum of the end ordinates plus four times the middle ordinate, all multiplied by one-sixth the increment of x, represents the value of the integral.

It is seen that the procedure outlined is exact if the function can be represented by a linear, quadratic, or cubic equation in the interval $x_3 - x_1$. If the curvature is great and the function complicated, the interval may be divided into a number of small intervals and the rule applied to each.

114. Numerical Integration. Gauss's Method. This method of integration, apparently not generally familiar to engineers, would appear to be particularly valuable in much chemical engineering work. By the use of three ordinates, it provides a means of obtaining the exact integral for a fifth-degree function, where Simpson's rule is exact only for a cubic. Values of the ordinate y are noted at n predetermined values of x. Each is multiplied by a predetermined constant and the sum of the products so obtained multiplied by the interval of x to give the desired integral. If n points are used, the method is exact if the function can be represented by a polynomial of the $(2n - 1)$th degree.

The derivation for the special case of a fifth-degree function will be developed briefly. The function is of the form

$$y = a_0 + a_1x + a_2x^2 + a_3x^3 + a_4x^4 + a_5x^5$$

When the substitution is made,

$$x = \frac{a + b}{2} + \frac{b - a}{2}u \tag{22}$$

the desired integral becomes

$$\int_a^b y\,dx = \frac{b - a}{2}\int_{-1}^{+1} y\,du = N(b - a) \tag{23}$$

where N is the average value of y over the interval a, b. Since y can be represented by a fifth-degree polynomial in x, it can also be represented by a similar function of u, such as

$$y = a_0' + a_1'u + a_2'u^2 + a_3'u^3 + a_4'u^4 + a_5'u^5 \tag{24}$$

Integrating (24) and substituting in (23) result in

$$N = a_0' + \frac{a_2'}{3} + \frac{a_4'}{5} \tag{25}$$

When the rule outlined is followed, this result may be obtained from three ordinates y_1, y_2, and y_3 and three constants K_1, K_2, and K_3, as follows:

$$N = K_1y_1 + K_2y_2 + K_3y_3 \tag{26}$$

where y_1, y_2, and y_3 correspond to values of x or u yet to be determined. From (26),

$$\begin{aligned} N = {} & K_1(a_0' + a_1'u_1 + a_2'u_1^2 + a_3'u_1^3 + a_4'u_1^4 + a_5'u_1^5) \\ & + K_2(a_0' + a_1'u_2 + a_2'u_2^2 + a_3'u_2^3 + a_4'u_2^4 + a_5'u_2^5) \\ & + K_3(a_0' + a_1'u_3 + a_2'u_3^2 + a_3'u_3^3 + a_4'u_3^4 + a_5'u_3^5) \\ = {} & a_0'(K_1 + K_2 + K_3) + a_1'(K_1u_1 + K_2u_2 + K_3u_3) \\ & + a_2'(K_1u_1^2 + K_2u_2^2 + K_3u_3^2) + a_3'(K_1u_1^3 + K_2u_2^3 + K_3u_3^3) \\ & + a_4'(K_1u_1^4 + K_2u_2^4 + K_3u_3^4) + a_5'(K_1u_1^5 + K_2u_2^5 + K_3u_3^5) \end{aligned} \tag{27}$$

If this is to be identical with the correct result (25), it is clearly necessary that the following relations hold:

$$\begin{aligned} K_1 + K_2 + K_3 &= 1 \\ K_1u_1 + K_2u_2 + K_3u_3 &= 0 \\ K_1u_1^2 + K_2u_2^2 + K_3u_3^2 &= \tfrac{1}{3} \\ K_1u_1^3 + K_2u_2^3 + K_3u_3^3 &= 0 \\ K_1u_1^4 + K_2u_2^4 + K_3u_3^4 &= \tfrac{1}{5} \\ K_1u_1^5 + K_2u_2^5 + K_3u_3^5 &= 0 \end{aligned}$$

These six equations may be solved to give numerical values for K_1, K_2, K_3, u_1, u_2, and u_3 as follows: $K_1 = K_3 = \frac{5}{18}$; $K_2 = \frac{4}{9}$; $u_1 = -\sqrt{\frac{3}{5}} = -0.7746$; $u_2 = 0$; $u_3 = \sqrt{\frac{3}{5}} = 0.7746$. Values of y corresponding to these values of u are multiplied by their respective K's and added together to give N, as shown by (26). The integral is $N(b - a)$, since N is the average value of y.

In general, a sufficient number of simultaneous equations are obtained to evaluate n K's and n values of u to be employed, where the polynomial is of the $(2n - 1)$th degree. Thus, four points are needed for an exact integration of a seventh-degree equation, etc. Although any number of seventh-degree curves could be drawn through the four points on the curve, they would necessarily all have the same area under them between $u = -1$ and $u = +1$.

The application of the method will appear much clearer if the simplicity of the change of variables is realized. All that is done is to change x to u so that the limits will be -1 and $+1$ instead of a and b.

As an example of the procedure, consider a simple case of a function which, for comparison, is easily integrated by the usual procedure. Let it be desired to obtain the integral

$$\int_0^2 y\,dx = \int_0^2 (10 + x - x^2 + x^3 - x^4 + x^5)dx \qquad (28)$$

On changing variables, it is apparent that $x = 0$ at $u = -1$; $x = 2$ at $u = 1$; $x = 1 - 0.7746 = 0.2254$ at $u = -\sqrt{\frac{3}{5}}$; $x = 1$ at $u = 0$; $x = 1.7746$ at $u = +\sqrt{\frac{3}{5}}$. The value of y at $u_1(x = 0.2254)$ is 10.27; y at $u_2(x = 1)$ is 11; and y at $u_3(x = 1.7746)$ is 31.9. The average value of the function is

$$N = \tfrac{5}{18} \times 10.27 + \tfrac{4}{9} \times 11.0 + \tfrac{5}{18} \times 31.9 = 13.8,$$

and the integral $(b - a)N$ is $2 \times 13.8 = 27.6$. This is identical with the value obtained by direct integration of (28).

Numerical values of u and of K to be used in applying the method are tabulated below for $n = 2$, 3, and 4, *i.e.*, when the integral is to be obtained from 2, 3, or 4 values of the function.

For $n = 2$

$$K_1 = K_2 = \tfrac{1}{2}; \qquad u_1 = -u_2 = \sqrt{\tfrac{1}{3}}$$

For $n = 3$

$$K_1 = K_3 = \tfrac{5}{18}; \qquad K_2 = \tfrac{4}{9}$$

$$u_1 = -\sqrt{\tfrac{3}{5}} = -0.7746 = -u_3; \qquad u_2 = 0$$

For $n = 4$

$$K_1 = K_4 = 0.1739; \qquad K_2 = K_3 = 0.3261$$

$$u_1 = -0.8611; \qquad u_2 = -0.34; \qquad u_3 = 0.34; \qquad u_4 = 0.8611$$

For $n = 5$

$$K_1 = K_5 = 0.118463; \qquad K_2 = K_4 = 0.239314;$$

$$K_3 = 0.284444$$

$$u_1 = -0.906180; \qquad u_2 = -0.538469; \qquad u_3 = 0$$

$$u_4 = 0.538469; \qquad u_5 = 0.906180$$

As pointed out above, these will give exact results for a cubic, fifth-, seventh-, and ninth-degree function, respectively, but may be used as approximations in other cases. The four-point method gives sufficient accuracy for most engineering work, and the three-point method may often be used to advantage.

Gauss's method of integration should be readily adaptable to engineering test work, where an observation is to be made frequently to obtain the average value of an important variable over the period of the test. As an example, it may be applied to flow measurements by Pitot tubes, to accomplish a simplification of the necessary traverse. In the usual case of a single traverse across one diameter of a round duct, the total fluid flow is given by

$$Q = \pi \int_0^{R^2} V d(r^2) = \frac{\pi R^2}{2} \int_{-1}^{+1} V d\left(\frac{r}{R}\right)^2 \tag{29}$$

As suggested on page 6, the integration may be obtained by plotting the velocities as obtained by the Pitot tube vs. r^2, or r^2/R^2, and integrating graphically. An alternative procedure is to measure the velocity at 10 points representing half-rings of equal areas, in which case the average velocity is one-tenth the sum of the 10 measured velocities. The readings are taken at values of r^2/R^2 of 0.1, 0.3, 0.5, 0.7, and 0.9, which correspond to 2.6, 8.2, 14.6, 22.6, 34.2, 65.8, 77.4, 85.4, 91.8, and 97.4 per cent of the distance from one wall to the other across a diameter.

If the three- or four-point Gauss methods are to be used, it must be possible to represent the velocity distribution in terms

TABLE XVII.—COMPARISON OF AVERAGE VELOCITIES CALCULATED BY VARIOUS METHODS

Test	Fluid	Duct diameter (ft.)	Fluid density (lb. per cu. ft.)	Average velocity (ft. per sec.)				Location of traverse
				By graphical integration	10 point	3-point Gauss	4-point Gauss	
A	Air	2.17	0.071	51.2	52.1	50.5	51.9	Air to preheater in billet reheater
B	Air	2.66	0.077	21.7	21.7	21.6	21.5	6 in. downstream from open inlet
C	Blast-furnace gas	6.33	0.078	62.0	62.3	63.9	61.7	19 diameters downstream from 45 deg. bend
D	Air	2.0	0.075	43.5	43.7	44.0	43.4	5 diameters downstream from right-angle bend
E	Air	1.05	0.073	25.1	25.2	25.1	25.3	4 diameters downstream from blower
F	Air	1.05	0.073	26.7	26.7	26.6	26.8	20 diameters downstream from right-angle bend
G	Water	0.33	62.3	10.9	10.9	10.9	10.8	25 diameters downstream from bend
H	Water	0.33	62.3	11.2	11.2	11.4	11.1	25 diameters downstream from bend
I	Sulfur-burner gas	1.46	0.076	23.8	23.8	24.2	23.7	34 diameters straight pipe upstream
J	Water	0.51	62.3	1.57	1.57	1.59	1.52	
K	Water	0.51	62.3	1.79	1.80	1.84	1.79	
L	Blast-furnace gas	3.0	0.078	13.5	13.5	13.6	13.5	Straight length of the gas main
M	Air	4.17	0.069	50.1	50.5	48.6	50.9	Immediately downstream from butterfly valve
N	Blast-furnace gas	2.0	0.077	57.1	57.4	57.1	58.5	3 diameters after one bend and just above another
O	Air	1.54	0.059	54.1	54.0	54.2	54.0	Downstream from a fan in a straight section
P	Hot air	1.5	0.053	39.6	39.6	39.9	39.6	8 diameters downstream and 2 diameters upstream from bends
Q	Air	1.94	0.075	39.0	39.2	39.6	39.0	
R	HCl air, 44% HCl	0.83	0.0829	27.5	27.6	27.6	27.6	5 diameters downstream from bend
Average percentage error as compared with graphical integration.....					0.25	1.1	0.8	

of position across the diameter by a fifth- or seventh-degree function. If the flow conditions result in a velocity distribution of such complexity that this is not possible, more points are needed for an exact result, and the simpler methods should be looked upon as approximations although they are usually sufficiently good for most plant test work. This is shown by the results of a number of Pitot-tube traverses obtained under widely different conditions in a steel plant, a paper mill, and a heavy chemical plant. The results of the three- and four-point Gauss integrations are compared in Table XVII with those of the 10-point method described above and with accurate graphical integrations. It will be noted that the comparison made is of the methods of integration only, and that the result will not be the true average velocity in the duct unless the flow in each half of the duct is symmetrical radially.

In making a simplified traverse as described, the problem is the integration from $-R$ to $+R$ of the area under a curve of V vs. r^2/R^2. If three points are used, the velocity is observed at the center ($u = 0$) and at $r^2/R^2 = -\sqrt{\frac{3}{5}}$ and $+\sqrt{\frac{3}{5}}$, *i.e.*, at the center and at two points at a radius of 0.880 R. The velocity at the center is multiplied by $\frac{4}{9}$, and the two other observed velocities are multiplied by $\frac{5}{18}$. The sum of the three products is the desired average velocity.

If four points are used, the readings are taken two at 0.928 R and two at 0.583 R. The two nearest the wall are multiplied by 0.1739, and the two nearest the center are multiplied by 0.3261. The sum of the four products is the average velocity in the duct.

115. Note on Numerical Integration. It must be remembered that any method of numerical integration is necessarily based on an adequate and representative *sampling* of the function to be integrated. The general nature of the function should be known, so that special attention may be paid any region in which y is suspected of varying rapidly or in a peculiar manner with x. If Simpson's rule is used, large increments of x may be taken in regions where the function is smooth and approximately linear, and small increments, with small values of h, employed in regions where the function changes rapidly.

Fortunately, in the natural processes encountered in most engineering work the functions are relatively simple, and the

danger is not great of failing to take a "sample" in a region where the function jumps rapidly. Methods of testing a function for its complexity by curve fitting with polynomials are discussed in another section (Pars. 108–111).

Simpson's rule involves multiplication of the ordinates sampled by simpler constants than does Gauss's method for equal accuracy, but the number of samples is larger and they must be chosen at equal intervals. For integration of algebraic functions Simpson's rule is usually to be preferred, but Gauss's method offers attractive possibilities for engineering test work.

Various other methods have been developed for numerical integration. Several of these are described and compared by Scarborough,* whose book should be consulted for a more complete discussion of the subject.

116. Interpolation. Interpolation is of practical importance to the engineer because of the constant necessity of referring to sources of information expressed in the form of a table. Logarithms, trigonometric functions, properties of steam, vapor pressures, and other physical and chemical data are commonly given in the form of tables in the standard reference works. Although these tables are sometimes given in sufficient detail so that interpolation is not necessary, it is important to be able to interpolate properly when the necessity arises.

It will be assumed that there is available a tabulation of a series of values of y for corresponding tabulated values of the independent variable x. The problem of interpolation is to obtain the correct value of y corresponding to some value of x lying between two tabulated values x_n and x_{n+1}. Extrapolation refers to the problem of finding a y corresponding to a value of x lying outside the range of tabulated values of x. The usual procedure in interpolation is to employ one of several formulas, these expressions being based on fitting a polynomial to the function represented by the table and then using the polynomial to calculate the desired value of y. The simplest illustration of the general method would be to fit two points y_0, x_0, y_1, x_1 by means of

$$y = a + bx$$

and then employ this equation to calculate y for some x lying between x_0 and x_1. Most engineers do this mentally when

* "Numerical Mathematical Analysis," Johns Hopkins Press, Baltimore, 1930.

reading values from the steam tables. If a number of points are used, the polynomial may be of a correspondingly high degree, and the method may be quite exact.

It may be noted that if the nature of the function is known it is foolish to apply an arbitrary polynomial, since the constants in the correct form may be obtained by substitution of a sufficient number of values of the variables. An exception to this statement may be the case of a complicated function difficult to evaluate numerically. In interpolation of values of vapor pressures, it is sometimes better to use the fact that the logarithm of the vapor pressure is very nearly linear in the reciprocal of the absolute temperature than to employ an interpolation formula.

Of the various interpolation formulas that are in standard use, only Newton's and Lagrange's will be described. For a discussion of the so-called "central-difference formulas" of Bessel and Stirling, the reader is referred to Scarborough, who summarizes the particular advantages and uses of the various forms. Newton's formula requires a table of values of y for equidistant values of the independent variable x. Lagrange's formula does not have this limitation.

117. Newton's Formula. In order to use Newton's interpolation formula, it is necessary to understand the construction of a *difference table*. The following is such a table, constructed from a series of values of y and x, where $y = x^3$:

TABLE XVIII.—DIFFERENCE TABLE

x	$y = x^3$	Δ^1	Δ^2	Δ^3	x	y	Δ^1	Δ^2	Δ^3
0.50	0.125				x_0	y_0			
		0.091					$\Delta^1 y_0$		
0.60	0.216		0.036		x_1	y_1		$\Delta^2 y_0$	
		0.127		0.006			$\Delta^1 y_1$		$\Delta^3 y_0$
0.70	0.343		0.042		x_2	y_2		$\Delta^2 y_1$	
		0.169		0.006			$\Delta^1 y_2$		$\Delta^3 y_1$
0.80	0.512		0.048		x_3	y_3		$\Delta^2 y$	
		0.217		0.006			$\Delta^1 y_3$		$\Delta^3 y_2$
0.90	0.729		0.054		x_4	y_4		$\Delta^2 y_3$	
		0.271		0.006			$\Delta^1 y_4$		$\Delta^3 y_3$
1.00	1.000		0.060		x_5	y_5		$\Delta^2 y_4$	
		0.331		0.006			$\Delta^1 y_5$		$\Delta^3 y_4$
1.10	1.331		0.066		x_6	y_6		$\Delta^2 y_5$	
		0.397					$\Delta^1 y_6$		
1.20	1.728				x_7	y_7			

The left half of the table shows the numerical values for the illustrative example; the right half of the table indicates the nomenclature used in referring to the various quantities. $\Delta^1 y_0$ is $(y_1 - y_0)$, and $\Delta^1 y_n$ is $(y_{n+1} - y_n)$.

$$\Delta^2 y_0 = \Delta^1 y_1 - \Delta^1 y_0 = (y_2 - y_1) - (y_1 - y_0) = y_2 - 2y_1 + y_0.$$

$$\Delta^2 y_n = \Delta^1 y_{n+1} - \Delta^1 y_n = (y_{n+2} - y_{n+1}) - (y_{n+1} - y_n) = y_{n+2} - 2y_{n+1} + y_n.$$

Similarly,

$$\Delta^3 y_0 = \Delta^2 y_1 - \Delta^2 y_0 = (y_3 - 2y_2 + y_1) - (y_2 - 2y_1 + y_0) = y_3 - 3y_2 + 3y_1 - y_0,$$

and $\Delta^3 y_n = y_{n+3} - 3y_{n+2} + 3y_{n+1} - y_n$.

It is apparent that in the case of the example the third differences are constant. It has already been seen that the first differences are constant for a linear equation, and it is not difficult to prove that the nth differences are constant for an nth degree polynomial, provided that the values of x are equidistant. This suggests the use of a difference table to determine the complexity of a function and the degree of the empirical polynomial that must be used.

The tabulated function is to be fitted by an nth degree polynomial, $f(x)$. This may be written

$$f(x) = a_0 + a_1(x - x_0) + a_2(x - x_0)(x - x_1) + a_3(x - x_0)(x - x_1)(x - x_2) + \cdots + a_n(x - x_0)(x - x_1) \cdots (x - x_{n-1}) \quad (30)$$

Substituting $f(x) = y_0$ at $x = x_0$, we get $a_0 = y_0$. Substituting $f(x) = y_1$ at $x = x_1$, we obtain

$$a_1 = \frac{y_1 - a_0}{x_1 - x_0} = \frac{\Delta^1 y_0}{h} \quad (31)$$

where h represents the constant x increment. If this process is continued the values of a_2, a_3, etc., are obtained as

$$a_2 = \frac{\Delta^2 y_0}{2h^2}; \qquad a_3 = \frac{\Delta^3 y_0}{3!h^3}; \qquad a_n = \frac{\Delta^n y_0}{n!h^n}$$

whence

$$f(x) = y_0 + (x - x_0)\frac{\Delta^1 y_0}{h} + (x - x_0)(x - x_1)\frac{\Delta^2 y_0}{2h^2} + (x - x_0)(x - x_1)(x - x_2)\frac{\Delta^3 y_0}{3!h^3} + \cdots + (x - x_0)(x - x_1) \cdots (x - x_n)\frac{\Delta^n y_0}{n!h^3}$$

Although this is the desired expression, it is usually rewritten in terms of another variable p defined by

$$p = \frac{x - x_0}{h}$$

whence

$$y = f(x) = y_0 + p\Delta^1 y_0 + \frac{p(p-1)}{2!}\Delta^2 y_0 + \frac{p(p-1)(p-2)}{3!}\Delta^3 y_0 + \frac{p(p-1)(p-2)(p-3)}{4!}\Delta^4 y_0 + \cdots + \frac{p(p-1)\cdots(p-n+1)}{n!}\Delta^n y_0 \quad (32)$$

Referring to the previous table, it will be noted that y_0, $\Delta^1 y_0$, $\Delta^2 y_0$, $\Delta^3 y_0$, etc., are the differences lying in the top diagonal column. It is apparent that these values are of significance primarily in the upper part of the table, and the formula (32), known as "Newton's formula for forward interpolation" (in the direction of increasing values of x), is best applied for interpolation near the first of the table.

The use of the formula may be illustrated by means of the numerical differences tabulated for x^3. Let it be desired to obtain the value of y for $x = 0.62$. Here $y_0 = 0.125$, $h = 0.10$, $p = 1.2$, $n = 3$; and the values of the differences are read from the table. Hence,

$$y = 0.125 + 1.2(0.091) + \frac{1.2(1.2-1)}{2}0.036 + \frac{1.2(1.2-1)(1.2-2)}{6}0.006 = 0.238328$$

In this case, the result is $(0.62)^3$ exactly since the function is of the third degree, the third differences are constant, and the interpolation formula included the term involving the third difference. Actually, the last term was quite small, and if only the second differences had been used the result would have been $y = 0.23852$. If the relation between y and x represents experimental data, the third or fourth differences may be only approximately constant, and the interpolation accordingly inexact. In using the interpolation formula, it should be noted that the accuracy of the result depends on the constancy of the last differences used as well as on the number of terms employed.

As another example, assume that it is desired to obtain the vapor pressure of water at 23°C. from a table of values given at 10° intervals. The difference table is prepared as shown below:

TABLE XIX

x (°C.)	y (mm. Hg)	Δ^1	Δ^2	Δ^3	Δ^4
10	9.21				
		8.33			
20	17.54		5.95		
		14.28		3.27	
30	31.82		9.22		1.20
		23.50		4.47	
40	55.32		13.69		1.52
		37.19		5.99	
50	92.51		19.68		1.78
		56.87		7.77	
60	149.38		27.45		
		84.32			
70	233.70				

The fourth differences not only are variable but show a definite trend, so the interpolation formula even including the Δ^4 term will be only an approximation. The result is

$$y = 9.21 + 1.3 \times 8.33 + \frac{1.3(1.3 - 1)}{2} \times 5.95 + \frac{1.3(1.3 - 1)(1.3 - 2)}{6} \times 3.27 + \frac{1.3(1.3 - 1)(1.3 - 2)(1.3 - 3)}{24} \times 1.20 = 21.07 \text{ mm. Hg}$$

This checks the correct value to within 0.01 mm., the result being good because several terms were calculated. Linear interpolation would give 21.82; if the formula were employed with only Δ^1 and Δ^2, the result would be 21.20.

If only the 20° and 30° values were available, the formula would reduce to linear interpolation. In such a case, it would be better to follow the procedure suggested above for interpolation of vapor-pressure data. From the Clausius-Clapeyron

equation, it follows that over moderate temperature ranges the logarithm of the vapor pressure is essentially linear in the reciprocal of the absolute temperature. At 20°, $\log p = 1.24403$, and $1/T = 1/293 = 0.003413$; at 30°, $\log p = 1.50276$, and $1/T = 0.003300$; at 23°, $1/T = 0.003378$, whence

$$\log p_{23} = 1.24403 + \frac{0.003413 - 0.003378}{0.003413 - 0.003300} \times (1.50276 - 1.24403)$$

$$p = 21.09 \text{ mm. Hg}$$

Although this method requires but two points, the calculation must be made quite carefully since the error is multiplied in taking the antilogarithm (see Chap. IX).

Perry's "Chemical Engineers' Handbook" tabulates vapor pressures of a large number of compounds. These are given as pressures at 10°C. temperature intervals or as temperatures for various values of p, and some method of interpolation is important for practical use. Either of the methods just described may be used, although Newton's formula probably gives the best results if a slide rule is used, provided that the third or fourth differences are included. It should be emphasized again, however, that the difference table must be built up using equidistant values of the independent variable.

118. Backward Interpolation. Referring again to the difference table for $y = x^3$ on page 279, we may follow the method of interpolation when y is desired for some value of x near the end of the table. If x lies between x_n and x_{n+1} and the kth differences are to be used, then we may replace $\Delta^1 y_0$, $\Delta^2 y_0$, etc., by the differences lying on a diagonal ending with the kth difference horizontally opposite x_n or x_{n+1}, depending on whether k is odd or even. For example, for $x = 1.06$, we use 0.271, 0.060, and 0.006 in place of $\Delta^1 y_0$, $\Delta^2 y_0$, and $\Delta^3 y_0$. Accordingly, y_0 is replaced by y_4, which is 0.729, and p is $(1.06 - 0.90)/h = 1.6$. This simply amounts to the omission of the tabulated values for x less than 0.9, and the construction of the difference table on the basis of the last four values tabulated.

If y is desired at $x = 1.16$, only Δ^1 is available for substitution in the formula. In this case, we resort to an inversion of the table, which then appears as follows:

TABLE XX

x	y	Δ^1	Δ^2	Δ^3
1.20	1.728			
		−0.397		
1.10	1.331		0.066	
		−0.331		−0.006
1.00	1.000		0.060	
		−0.271		−0.006
0.90	0.729		0.054	
		−0.217		−0.006
0.80	0.512		0.048	
		−0.169		
0.70	0.343			
	etc.			

Using this inverted table, we may proceed in the usual way employing the values of y and Δ in the top diagonal row for substitution in the formula. In terms of the original nomenclature the formula becomes

$$y = y_7 + q\Delta^1 y_7 + \frac{q(q+1)}{2!}\Delta^2 y_6 + \frac{q(q+1)(q+2)}{3!}\Delta^3 y_5 + \cdots \frac{q(q+1)(q+2)\cdots(q+n-1)}{n!}\Delta^n y_{8-n}$$

where

$$q = \frac{x - x_7}{h}$$

In general, where x_n, y_n are the last values given, interpolation near the end of the table may be carried out by substitution in the general form.

$$y = y_n + q\Delta^1 y_n + \frac{q(q+1)}{2!}\Delta^2 y_{n-1} + \frac{q(q+1)(q+2)}{3!}\Delta^3 y_{n-2} + \cdots \frac{q(q+1)(q+2)\cdots(q+n-1)}{n!}\Delta^k y_{n-k+1} \quad (33)$$

where $q = \dfrac{x - x_n}{h}$. In the case of $x = 1.16$, this gives

$$y = 1.728 - 0.4 \times 0.397 - \frac{0.4 \times 0.6}{2} \times 0.066 - \frac{0.4 \times 0.6 \times 1.6}{6} \times 0.006$$

$$= 1.560896.$$

119. Lagrange's Interpolation Formula. The construction of a difference table and the use of Newton's formula have the advantage that the relative constancy of the last differences is immediately apparent and the accuracy of the interpolation indicated qualitatively in this way. The quantitative error may be calculated quite accurately by equations expressing the error in terms of the differences tabulated. The method has the disadvantage, however, of being limited to tabulated values of x, which are equidistant.

As before, it is assumed that the function may be represented by a polynomial, now written in the form

$$\begin{aligned} y = {} & a_1(x - x_2)(x - x_3)(x - x_4) \cdots (x - x_n) + \\ & a_2(x - x_1)(x - x_3)(x - x_4) \cdots (x - x_n) + \\ & a_3(x - x_1)(x - x_2)(x - x_4) \cdots (x - x_n) + \\ & \cdots a_n(x - x_1)(x - x_2)(x - x_3) \cdots + (x - x_{n-1}) \end{aligned} \quad (34)$$

Substituting y_1, x_1, we have

$$a_1 = \frac{y_1}{(x_1 - x_2)(x_1 - x_3)(x_1 - x_4) \cdots (x_1 - x_n)}$$

The other constants are obtained by similar substitutions, and

$$a_n = \frac{y_n}{(x_n - x_1)(x_n - x_2)(x_n - x_3) \cdots (x_n - x_{n-1})} \quad (35)$$

Rewriting the polynomial gives

$$\begin{aligned} y = {} & y_1 \frac{(x - x_2)(x - x_3)(x - x_4) \cdots (x - x_n)}{(x_1 - x_2)(x_1 - x_3)(x_1 - x_4) \cdots (x_1 - x_n)} + \\ & y_2 \frac{(x - x_1)(x - x_3)(x - x_4) \cdots (x - x_n)}{(x_2 - x_1)(x_2 - x_3)(x_2 - x_4) \cdots (x_2 - x_n)} + \cdots + \\ & y_n \frac{(x - x_1)(x - x_2)(x - x_3) \cdots (x - x_{n-1})}{(x_n - x_1)(x_n - x_2)(x_n - x_3) \cdots (x_n - x_{n-1})} \end{aligned} \quad (36)$$

As an example of the use of Lagrange's formula, let it be desired to obtain the density of a 26 per cent solution of phosphoric acid in water at 20°C. The following data are quoted by Perry:

y (density)	1.0764	1.1134	1.2160	1.3350
x (percentage H_3PO_4)	14	20	35	50

It is obvious that we may apply the interpolation formula to the figures after the decimal point, replacing the 1 at the end of the calculation. Substituting in (36), we have

$$y = 1.0 + 0.0764\frac{(26-20)(26-35)(26-50)}{(14-20)(14-35)(14-50)} + 0.1134\frac{(26-14)(26-35)(26-50)}{(20-14)(20-35)(20-50)} + 0.2160\frac{(26-14)(26-20)(26-50)}{(35-14)(35-20)(35-50)} + 0.3350\frac{(26-14)(26-20)(26-35)}{(50-14)(50-35)(50-20)}$$

$$= 1.0 - \frac{2}{7} \times 0.0764 + \frac{24}{25} \times 0.1134 + \frac{64}{175} \times 0.2160 - \frac{1}{25} \times 0.3350$$

$$= 1.1528$$

This may be compared with the correct value 1.1529, given in the same table from which the data quoted above were obtained.

In the example given, four tabulated points were used, which means that the interpolation is based on fitting the function with a cubic equation. The accuracy of the result naturally depends on how well such an equation fits the data, and this should be kept in mind in using Lagrange's formula. In the case of vapor-liquid equilibrium data for binary mixtures, the vapor composition is related to the liquid composition by a function frequently too complex to be interpolated by means of Lagrange's formula with only four points. This is particularly true in the case of azeotropic mixtures. A large number of points are required for interpolation of functions having points of inflexion. When the formula is employed, the arithmetic may be tested if we note that the coefficients of y_1, y_2, etc., must add to unity, since the formula must hold true if all values of y are equal.

120. Numerical Differentiation (see also Par. 6). Since the interpolation formulas represent polynomials passing through the tabulated points, they may be differentiated to obtain approximate derivatives of the function. The process of obtaining the derivatives, however, will usually be less accurate than in representing the function by the polynomial. The error becomes greater with each successive differentiation.

As an illustration we may differentiate Newton's formula (32), as follows:

$$\frac{dy}{dx} = \frac{dy}{dp} \cdot \frac{dp}{dx} = \frac{1}{h}\frac{dy}{dp} = \frac{1}{h}\left[\Delta^1 y_0 + \frac{2p-1}{2!}\Delta^2 y_0 + \frac{3p^2 - 6p + 2}{3!}\Delta^3 y_0 + \frac{4p^3 - 18p^2 + 2p - 6}{4!}\Delta^4 y_0 \cdots \right] \quad (37)$$

Referring to the difference table for x^3 on page 279, we may substitute in the foregoing expression to obtain the derivative at $x = 0.62$ $(p = 1.2)$

$$\frac{dy}{dx} = \frac{1}{0.1}\left[0.091 + \frac{2 \times 1.2 - 1}{2} \times 0.036 + \frac{3(1.2)^2 - 6 \times 1.2 + 2}{6} \times 0.006 \right]$$

$$= 1.1532$$

In this case, the function is a simple polynomial, and the result, consequently, is exact.

The same general procedure may be applied to any of the interpolation formulas, although in the case of experimentally determined functions it is usually desirable to employ six or seven points if the derivative is to be obtained with slide-rule accuracy. The accuracy of the derivative obtained by any method will obviously vary widely with the complexity of the functions. If the values of x are not equidistant, we may differentiate Lagrange's formula, but the resulting numerical calculations are rather tedious.

121. Douglass-Avakian Method of Numerical Differentiation. The procedure just outlined involves fitting n points exactly by a polynomial of the $(n-1)$th degree and then taking the derivative. An alternative procedure, developed by Douglass and Avakian, employs a fourth-degree polynomial, which is fitted to seven points by the methods of least squares. The values of the independent variable are necessarily equidistant, and the origin is arbitrarily taken at the central value. The polynomial is

$$y = a + bx + cx^2 + dx^3 + ex^4$$

and the values of the constants a, b, c, d, and e are given by the expressions (12) to (16) on page 267. The slope of the poly-

nomial at the central point ($x = 0$) is b, so that the derivative may be obtained directly from the equation

$$\frac{dy}{dx} = b = \frac{397\,\Sigma ky}{1{,}512h} - \frac{7\,\Sigma k^3 y}{216h} \tag{38}$$

provided that values of the function are chosen at three points equally spaced on either side of the point where the derivative is desired. The method is exact, provided that the function can be represented by a fourth-degree, or simpler, polynomial, and gives good results in other cases if the function is not too complicated. It has the great advantage of simplicity, involving relatively little calculation.

Referring again to the function $y = x^3$, let it be desired to obtain the derivative at $x = 0.80$. The following table is easily constructed:

TABLE XXI

x	y	k	ky	k^3y
0.50	0.125	−3	−0.375	−3.375
0.60	0.216	−2	−0.432	−1.728
0.70	0.343	−1	−0.343	−0.343
0.80	0.512	0	0	0
0.90	0.729	1	0.729	0.729
1.00	1.000	2	2.000	8.000
1.10	1.331	3	3.993	35.927
			5.572	39.210

whence

$$\frac{dy}{dx} = \frac{397 \times 5.572}{1{,}512 \times 0.1} - \frac{7 \times 39.210}{216 \times 0.1} = 14.62 - 12.70 = 1.92$$

which, in this case, is exact because the function can be fitted exactly by a fourth-degree polynomial.

Practical use of this method shows that it gives somewhat better results and requires about the same time as the graphical determination using a good protractor. It has many obvious applications in chemical engineering, such as the determination of various differential coefficients from thermodynamic data, the analysis of drying curves to obtain instantaneous drying rates, etc.

CHAPTER VIII

GRAPHICAL TREATMENT OF CHEMICAL ENGINEERING PROCESSES

122. Uses of Graphical Methods. Graphical methods have proved invaluable in the analysis of the relatively complex processes with which the chemical engineer deals. Much of the basic physical and chemical data is best represented graphically, and graphical methods are introduced in this way into the analytical treatment of the process.

One or more of the many types of graphical representations may be employed for the following purposes: (1) as an aid in visualizing a process or the meaning of a computation, (2) for the representation of quantitative data, or of a theoretical or empirical equation, (3) for the comparison of experimental data with a theoretical or empirical expression, (4) as a means of computation. Diagrammatic flow sheets are familiar and invaluable aids in visualizing industrial chemical processes and as shorthand representations of plant layouts. Most student engineers form the valuable habit of making a diagrammatic sketch before starting any numerical computation, whether it be a simple heat or material balance or a complicated plant design. Such diagrams are not drawn to scale, the sketch serving merely to put and keep ideas in mental order. When used in connection with an energy balance, for example, a simple sketch may serve as a reminder of energy inputs or outputs, which might otherwise be overlooked, and as a ready check of the signs of the terms in the expression equating total input to output.

123. Graphical Representation of Data or of an Equation. The relation between two physical quantities p and x is commonly obtained as a tabulation of values of p for a number of different values of x. The relation between p and x is not easy to visualize by studying the tabulated results and is best seen by plotting p vs. x. If the conditions of the experiment are such that p is known to be a function of x only, the functional relation will be indicated by the fact that the points may be represented

graphically by a smooth curve, and deviations of the points from a smooth curve indicate the reliability of the data. If p is a function of two variables x and y, a series of results of p in terms of x may be obtained for each of several values of y. When plotted, the data will be represented by a family of curves, each curve representing the relation between p and x for a definite constant value of y. If another variable z is involved, we may have separate graphs for constant values of z, each showing a family of curves of p vs. x. Extension of this method of representing data to relate more than four quantities is impractical unless general relations between two or more of the variables can be obtained. This point is discussed further below.

The ordinary graphical representation of experimental results is usually the first step in finding an empirical equation to represent the data, as described in the preceding chapter. Even when the empirical equation is to be obtained directly from the tabulated data by a numerical process, it is usually desirable to plot the points in order that the nature of the function may be visualized. Where the calculated relation between two quantities is dependent wholly on sound theoretical or empirical equations, it may be desirable to plot the resulting function in order to visualize its properties. As pointed out in Chap. I, the result of an economic balance calculation may frequently be obtained without the use of a graph, but a graph of the final calculation of costs may be quite helpful. Thus, where costs are obtained in terms of some variable x, a graph of costs vs. x may bring out the point that the optimum is not sharp, and that operation at a value of x somewhat different from the true optimum may permit of a considerably smaller investment with little change in total annual charges.

124. Choice of Coordinate Scales. The use to which the graph is to be adapted should be kept in mind in preparing a graphical representation either of data or of an equation. The coordinates should be chosen in such a way that the accuracy of reading the graph will be good for all ranges of the variables involved, with the resulting curve falling with a slope of roughly ± 1 on a square diagram. As an example, we may consider a plot of E vs. τ for the unsteady-state cooling of an infinite solid slab, for the case of an infinite surface coefficient. The relation between E and τ was obtained in Par. 99 as

$$E = \frac{8}{\pi^2}\left(e^{-\left(\frac{\pi}{2}\right)^2\tau} + \frac{1}{9}e^{-9\left(\frac{\pi}{2}\right)^2\tau} + \frac{1}{25}e^{-25\left(\frac{\pi}{2}\right)^2\tau} + \cdots\right) \quad (1)$$

where E represents the heat content of the slab at any time as a fraction of the heat content at the start of the cooling, both computed with reference to the constant surface temperature. It is clear that values of E may be obtained directly for any value of τ, but a tedious trial-and-error calculation is necessary if τ is to be obtained for a given value of E. By means of a graph of E vs. τ, we may read E in terms of τ or τ in terms of E with equal facility.

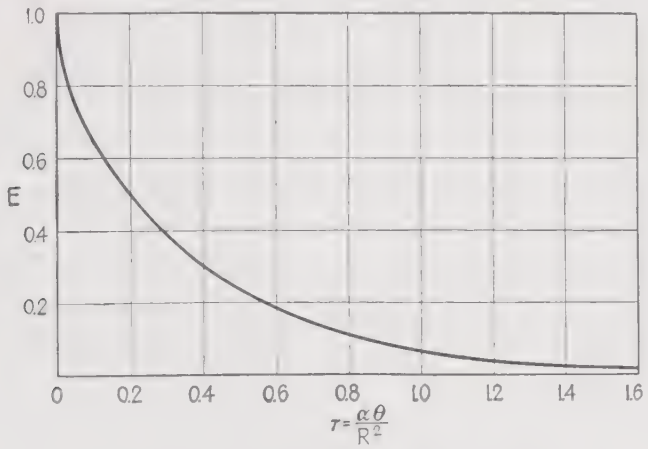

FIG. 72.—Ordinary graph of E-τ function.

Figure 72 shows E plotted vs. τ on ordinary rectangular coordinate paper. It is apparent that τ cannot be read accurately for large values of E, nor can E be obtained accurately at large values of τ. When τ is large, the first term of the series is the only one of significance and the series reduces to an exponential relation, suggesting a graph of log E vs. τ or a graph of E vs. τ on semilogarithmic coordinate paper. Figure 73 is such a graph of E vs. τ, with a logarithmic ordinate scale and a linear abscissa scale. It is apparent that this method of plotting represents a considerable improvement, as the graph may be read with good accuracy (in view of its size) except for small values of τ. Figure 74 represents a further modification of the same graph. The logarithmic scale from $E = 0.6$ to $E = 1.0$ has been doubled and a larger abscissa scale used in this region. The result is a combination of two graphs similar to Fig. 73.

with different ordinate and abscissa scales for values of E greater and less than 0.6. The two graphs are fitted together, giving a curve with two branches. The accuracy in reading values

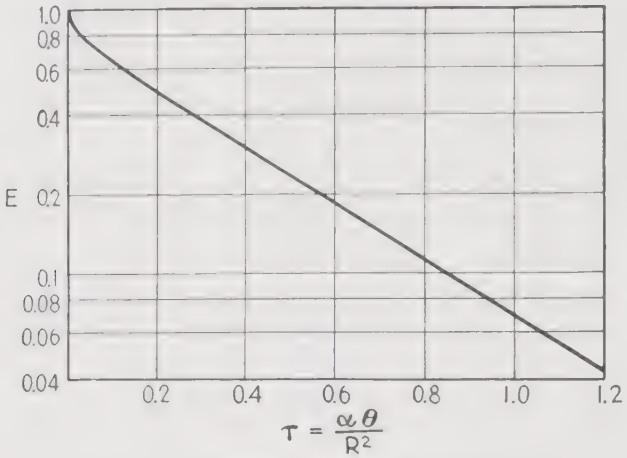

FIG. 73.—Semilog graph of E-τ function.

from branch A is considerably improved, although the accuracy at large values of τ is less than in Fig. 73.

125. Elimination of Trial and Error. Experimental data or correlations of experimental data should be plotted, if possible,

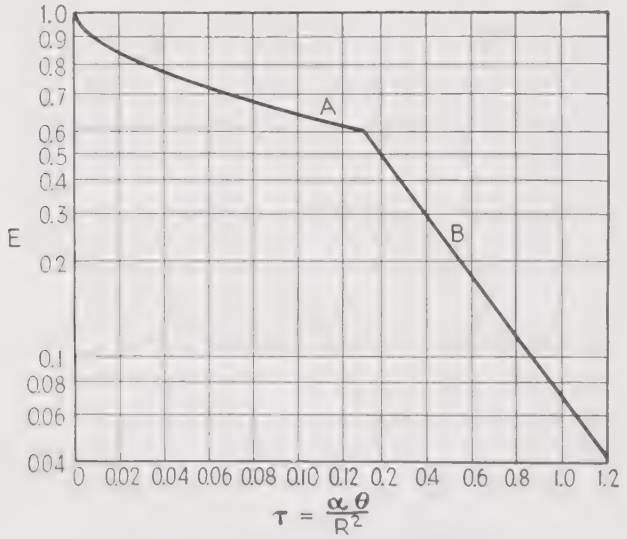

FIG. 74.—Extended abscissa scale.

so that the use of the graph should eliminate trial-and-error calculations. This is not always possible for all uses to which the graph may be adapted, but alternative methods of plotting

may be used to advantage in using the data in different ways. The familiar friction-factor graph for fluids in round pipes represents a correlation of a large amount of data, usually plotted as f vs. $DV\rho\ \mu$ with logarithmic ordinate and abscissa scales (Fig. 75). This is used in connection with the Fanning equation

$$H = \frac{2fLV^2}{gD} \tag{2}$$

where H represents the head lost due to friction in a length L of pipe having a diameter D, g is the acceleration due to gravity,

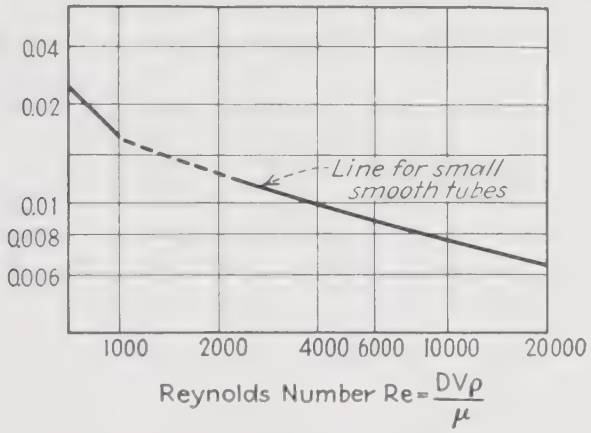

FIG. 75.—Usual friction-factor graph.

V is the superficial fluid velocity, ρ is the fluid density, μ the fluid viscosity, and f the dimensionless friction factor. When all quantities are known except the head loss H, which is to be calculated, the group Re is first obtained, f read from the plot, and H calculated directly from the equation. If it is desired to calculate the necessary pipe diameter for a specified flow and head, the problem becomes one of trial and error, since the Reynolds group is not immediately obtainable. Similarly, trial and error is involved in the calculation of the flow to be expected with a specified head, fluid, and pipe size. It is clear that the method of plotting is inconvenient for two of the three usual calculations in connection with which the correlation is of value.

For the problem of calculating the pipe diameter, we may proceed to find a method of plotting the data that will eliminate

the time-consuming trial and error. Let Q represent the volume rate of flow, whence

$$Q = \frac{\pi}{4} D^2 V$$

Combining with (2) and solving for D, we have

$$D^5 = \frac{32fLQ^2}{\pi^2 g H} = af \tag{3}$$

where a is substituted for the group of known quantities. Similarly, if the expression for Q is substituted in the Reynolds group and D separated, we have

$$D = \frac{4}{\pi} \frac{Q\rho}{\mu Re} = \frac{b}{Re} \tag{4}$$

where b is substituted for $4Q\rho \ \pi\mu$ and which involves only quantities specified in the problem. Eliminating D between the last two relations, we have

$$\frac{b^5}{a} = f(Re)^5; \qquad \text{or} \qquad \frac{b}{\sqrt[5]{a}} = Re\sqrt[5]{f} \tag{5}$$

The result is an expression for a function of f and Re, the coordinates of the graph, in terms of quantities in the problem of finding D. From the graph of f vs. Re, we may construct a graph of $Re\sqrt[5]{f}$ as abscissa with either f or Re as ordinate. With such a graph available, $Re\sqrt[5]{f}$ is calculated from the data given, and D calculated from the observed ordinate f or Re. Figure 76 shows the curve of Fig. 75 replotted as $Re\sqrt[5]{f}$ vs. Re, for use in this way. It is clear that a plot of $f(Re)^5$ vs. Re or f would serve equally well.

Since Re appears in both variables plotted, the calculated value of D is quite insensitive to f. This is true because of the relation between the variables and not because of the method of plotting, although it will be shown below that graphical representations of data should not, in general, involve the same variable in both ordinate and abscissa.

Following the same principle of eliminating the variable to be determined from one of the quantities plotted, it may be shown that the third calculation to determine the flow for a specified head and pipe size is easily carried out using a plot of $Re\sqrt{f}$ vs. Re or f. Walker, Lewis, McAdams, and Gilliland give a plot of this type.

123. Misleading Methods of Correlation. Any correlation of experimental data based on a graph in which the same variable appears in both ordinate and abscissa should be viewed with suspicion. When one of the less important variables is placed in both quantities plotted, it is possible to extend the scale and make the correlation appear to be much better than it really is.

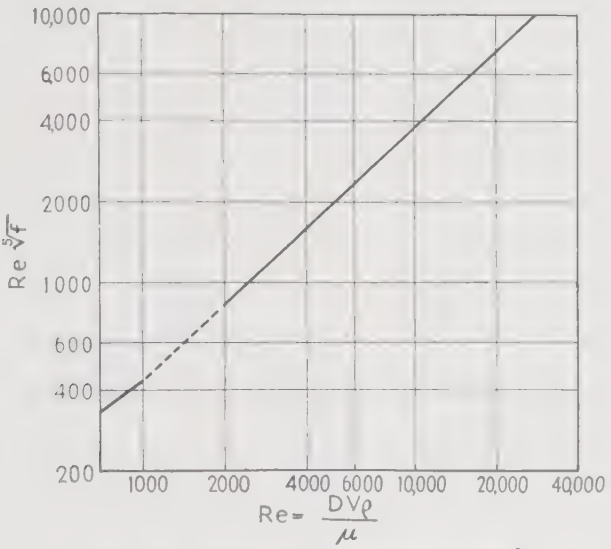

FIG. 76.—Modified friction-factor graph.

As an example, consider the following data, which we may imagine to have been obtained in an experimental study of the operation of a bubble-cap rectifying column. The plate efficiency E was obtained at various values of the superficial vapor velocity V and the liquor rate L across the plate.

TABLE XXII

E, plate efficiency (per cent)	V, vapor velocity (ft. per sec.)	L, liquor rate (lb. per min.)
22	0.5	100
44	1.1	20
60	0.8	40
70	2.4	80
78	2.1	32
85	1.3	55

Figures 77 and 78 show that there is no apparent correlation between E and V or E and L. However, if log $(EL)^3$ is plotted vs. log (VL^3) as shown in Fig. 79, what appears to be a good correlation is obtained because variations in L^3, appearing in

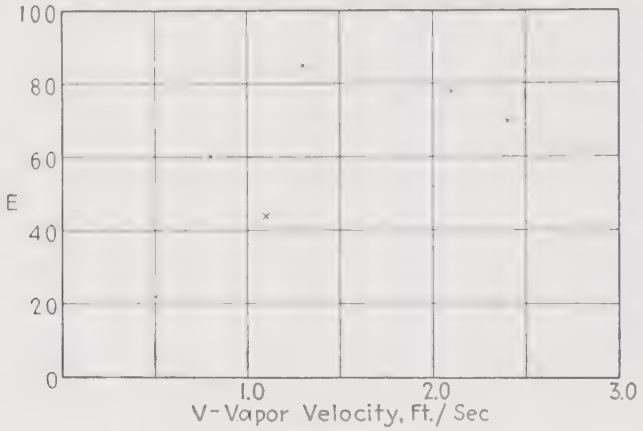

FIG. 77.

both variables, greatly overshadow variations in E and V. As a matter of fact, a geometric mean value of E of 0.55 would represent the data practically as well as the solid line shown. The dotted line of Fig. 79 represents this value of E, with V taken as 1.0 in order to plot.

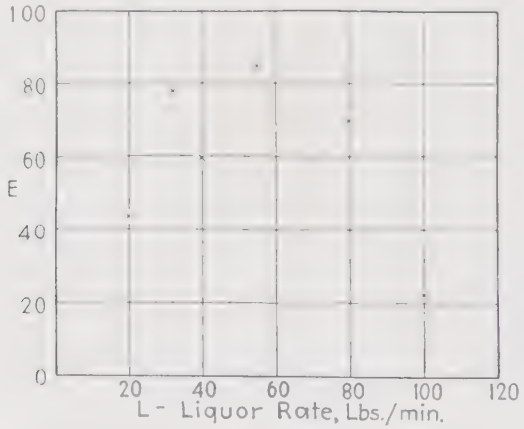

FIG. 78.

Correlations of experimental data based on graphs similar to Fig. 79 are occasionally presented in the literature. The investigator, trying various methods of plotting his results, hits upon a method of plotting that brings his data together and presents a

correlation that is unintentionally deceiving as to its generality. Such methods of plotting may be arrived at by fairly sound analysis of the physical problem involved and may be defended as being rational, although a poor test of the data. A rather subtle example of this process arises in the study of heat transfer to boiling liquids. The surface coefficients obtained are large and are relatively difficult to reproduce, so that the problem of correlating such data is difficult. Let us suppose a set of data to have been obtained, covering a range of temperature differences between steam and boiling water in an evaporator relying on liquid circulation by natural convection. The experimenter is confronted with a series of values of h and Δt, all the results having been obtained with a constant liquid composition and boiling temperature. He reasons that the surface coefficient of heat transfer is dependent on

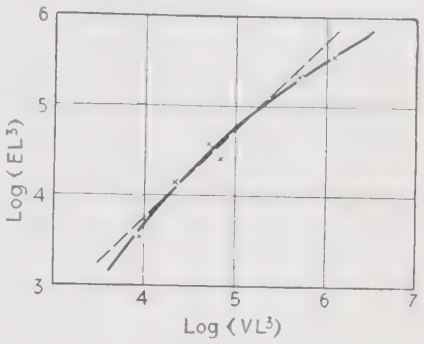

FIG. 79.

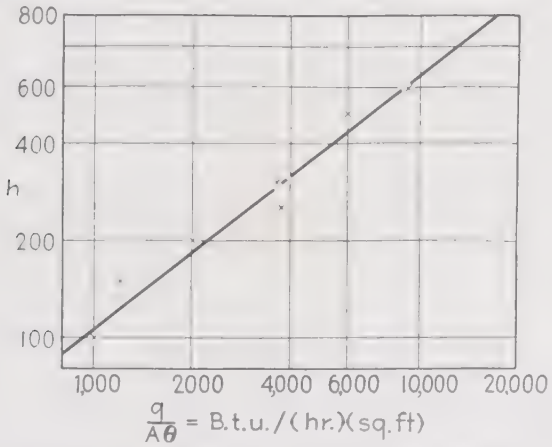

FIG. 80.—Correlation of data on heat transfer.

the effective thickness of some type of surface film and that this in turn should be a function of the degree of agitation of the liquid in the evaporator. The agitation should be a function of the rate of boiling and the rate of heat transfer in turn. He reaches the conclusion, therefore, that h should depend on the heat "current density" $q/A\theta$ and prepares a graph to test this conclusion. The

result is shown in Fig. 80, which indicates a better correlation than is often obtained for this case of heat transfer.

It should be noted, however, that the abscissa q $A\theta$ is the calculated product of h and Δt, and the graph, therefore, involves h in both ordinate and abscissa. If h is plotted vs. Δt, the result indicates a poor correlation of the data, as shown by Fig. 81. Fundamentally, the two graphs, Fig. 80 and 81, are equivalent, but the former appears to present a better correlation of the data because large variations in h overshadow small deviations of Δt.

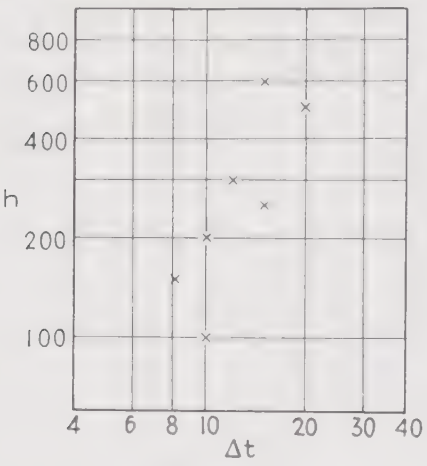

FIG. 81.

It may be argued that the quantities varied were the rate of heat flow and the steam temperature and that these should be the variables plotted, but general correlations on such a basis would be inconvenient; and the graph of h vs. Δt is an excellent test of the experimental data.

From the example quoted above, it follows that if one variable plotted is *divided* by some function of the other, a graph of the resulting ratio may present a more severe test of the data. For example, in plotting results of fluid-flow experiments, we have

$$f = \frac{\pi^2 H g D^5}{32 L Q^2}$$

and

$$Re = \frac{4Q\rho}{\pi\mu D}$$

If the experimental variables are H and D, with L, Q, μ, and ρ held constant, the graph of f vs. Re is really a graph of HD^5 vs. $1/D$. If the measured value of D is 10 per cent too great but H correct, the abscissa will be 9 per cent too small, and the ordinate will be 61 per cent high. The general slope of the curve is negative, and the experimental point will be considerably off. In this case, the method of plotting represents a severe test of the data. If the experimental variables are H and ρ, all others being held constant, then the usual friction-factor graph

represents a direct plotting of the variables studied. When a number of variables are to be related, it is seldom possible to find a single method of plotting that will represent an equally critical test of the experimental data relating various pairs of the variables.

127. Logarithmic and Semilogarithmic Graph Paper. The graphical representation of data may frequently be simplified by the use of various special types of coordinate paper, the commonest being logarithmic and semilogarithmic graph papers. The former, used in Fig. 80, has logarithmic scales for both ordinate and abscissa. The latter has a logarithmic ordinate scale and a linear abscissa scale. Both are widely used in chemical engineering because of the frequency with which experimentally determined relations appear in the forms $y = ax^n$ or $\log y = a + bx$. The former is represented by a straight line on logarithmic paper, and the latter by a straight line on semilogarithmic paper (see Par. 108). Straight-line representations of experimental data are to be desired as simplifying approximate graphical interpolation and extrapolation. Furthermore, a line may readily be placed to represent experimental points if the indicated relation is linear.

A logarithmic scale for the variable y is a linear scale for $\log y$. Instead of being labeled by numbers at equal intervals representing equal increments of $\log y$, it is labeled in terms of the antilog y. Equal linear increments on such a scale represent equal increments of $\log y$, and hence equal *percentage changes* in y. Since the eye tends to judge the trend of a curve by estimating the displacement linearly, a percentage change is best visualized by the use of a logarithmic scale. For this reason, semilogarithmic graphs have become popular in representing financial data, business trends, etc., where the percentage change rather than the numerical change is considered important. The abscissa is usually time plotted by the use of a linear scale.

If a logarithmic scale is used, a definite percentage deviation of an experimental point from a line is represented by a definite linear distance on the graph, no matter what region of the graph may be considered. If the ordinate of the point is y' and the ordinate of the curve is y, then the deviation as represented by the distance between the point and the line is $\log y' - \log y$, or $\log [1 + (y' - y)/y]$. Since the percentage deviation is

$$(y' - y)/y \times 100$$

it follows that there is a fixed relation between percentage deviation and linear deviation as represented by the actual distance on the graph paper between the point and the line. This valuable property of the logarithmic scale is of importance in plotting data, reading a graph, or in comparing a series of plotted points with a line representing a function. It may be contrasted with ordinary rectangular coordinate paper, on which a 10 per cent deviation of a point from a line may be too small to notice

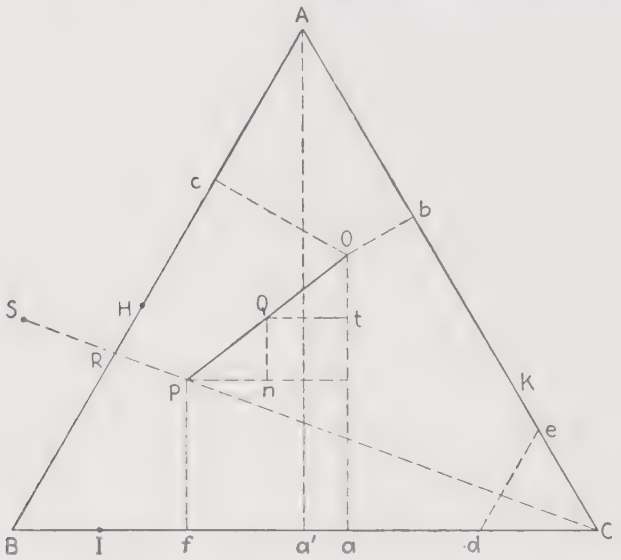

FIG. 82.—Triangular-coordinate graph.

if the point is near the origin, and may be represented by a linear distance of an inch or two if the value of the variable is large.

128. Triangular Graph Paper. Triangular graph paper is of value for various special purposes and has come into use in recent years in connection with the chemical engineering operations of crystallization, leaching, extraction, and distillation. Examples of its use for computations in these fields will be given later, but its general properties may be outlined at this point. Figure 82 represents the equilateral triangle used. It is easy to show that the sum of the perpendiculars from any point O to the three bases is equal to the length of a perpendicular from any apex to the opposite base, *i.e.*, that $Oa + Ob + Oc = Aa'$.

If the length Aa' is 100 units, then the composition of a three-component mixture may be represented by a point O, the percentage of component A being represented by the length of the perpendicular Oa, the percentage of component B by Ob, etc. The scales may be marked off, so that the lengths of the perpendiculars may be read directly and need not be measured. Alternatively, it may be shown that the combined lengths of the three lines extending from any point P to three sides of the triangle, in directions parallel to three other sides, are equal to the length of one side; and this property may be made the basis of representing the three percentages. For example in Fig. 82, $PH + PI + PK = AB$. Lines may be plotted for various purposes; equilibrium data for a ternary liquid mixture may be represented by lines of constant temperature for a given total vapor pressure. The compositions of a large number of coals, lignites, etc., when plotted on a triangular plot show clusters of points indicating distinct groups of fuel types. This graph with the three components taken as carbon, hydrogen, and oxygen (moisture- and ash-free basis) represents one basis for the classification of coals. The graph used represents one corner of the complete triangle, one apex representing 100 per cent carbon and the other two representing perhaps 20 per cent oxygen and 20 per cent hydrogen. If Fig. 82 represents the complete triangle, only the section Cdc would need to be reproduced in plotting the fuel compositions.

The fact that the sum of the perpendiculars from any point to the three sides is equal to the altitude of the triangle makes it possible to represent compositions of ternary mixtures graphically and is one of two important properties of the triangular graph. The other property of interest is that the point representing the composition of a mixture of two materials O and P will lie on a straight line connecting the two points representing the compositions of the two materials O and P. Furthermore, the location of the point representing the mixture bears a simple relation to the amounts of O and P mixed. Referring to Fig. 82, suppose a weight W_o of the material O is mixed with a weight W_p of the material P. Let the composition of O be x_o, y_o, and z_o and the composition of P be represented by x_P, y_P, and z_P, where x, y, and z represent the weight fractions of the pure

components A, B, and C. Using a similar nomenclature for the mixture Q, we may write the material balances

$$W_P x_P + W_0 x_0 = (W_P + W_0) x_Q \tag{6}$$

and

$$W_P y_P + W_P y_0 = (W_P + W_0) y_Q \tag{7}$$

Since z is fixed, if x and y are fixed, a balance on component C represents merely an addition of (6) and (7). The balances (6) and (7) may be rewritten as

$$W_P(x_P - x_Q) = W_0(x_Q - x_0) \tag{8}$$

and

$$W_P(y_P - y_Q) = W_0(y_Q - y_0) \tag{9}$$

which may be combined to give

$$\frac{x_0 - x_Q}{x_Q - x_P} = \frac{y_0 - y_Q}{y_Q - y_P} \tag{10}$$

It is not difficult to show* that for any straight line OP on a triangular graph, the length cO is a linear function of the distance Ba. From this, it follows that the equation of a straight line on a triangular graph is of the form

$$y = ax + b$$

where y and x represent any two perpendiculars or any two of the three quantities representing the compositions. The straight line OP is represented by the equations

$$y_P = ax_P + b$$
$$y_0 = ax_0 + b$$

* Place the side BC coincident with the x' axis and apex B at the origin of a set of rectangular coordinates (x', y'). Then the equation of PO referred to the rectangular axes is

$$y' = mx' + b$$

but at any point O, (x', y'), on this line

$$Oc = z = (x' \tan 60° - y') \cos 60°$$

and

$$y' = m\left(\frac{z + y' \cos 60°}{\cos 60° \tan 60°}\right) + b$$

Since $y' = Oa = x = 1 - z - y$, this equation indicates that any two perpendiculars from a point within the triangle to its sides, or any two of the three quantities representing the compositions, are related linearly.

which may be solved for a and b, and the equation written

$$y = \left(\frac{y_P - y_0}{x_P - x_0}\right)x + y_P - \left(\frac{y_P - y_0}{x_P - x_0}\right)x_P$$

or

$$\frac{y - y_P}{x - x_P} = \frac{y_P - y_0}{x_P - x_0} \tag{11}$$

This may easily be shown to be identical with (10), with x, y replacing x_Q, y_Q. It follows that the point Q representing the mixture of P and Q must lie on the straight line OP.

Furthermore, from (9) and (10) it follows that

$$\frac{W_P}{W_0} = \frac{x_0 - x_Q}{x_Q - x_P} = \frac{Ot}{Qn} = \frac{OQ}{PQ} \tag{12}$$

which means that not only is the point Q on the straight line PO, but the distances of Q from the points O and P are in inverse ratio to the amounts of O and P mixed to give Q. The use of this rule in handling the stoichiometry of mixtures of three-component systems will be illustrated later in the chapter by several examples.

It should be evident that the construction applying to mixtures also applies to the separation of two quantities. Thus, if a certain amount of the material P is removed from a mixture Q, there will remain a mixture of some material O. Point P represents a mixture containing 30 per cent A, 55 per cent B, and 15 per cent C. If all of the pure component C is removed, the resulting mixture is represented by point R and contains 35.3 per cent A and 64.7 per cent B. Although we may physically remove no more than 15 parts of C from the mixture P, we may go through the algebraic process of removing more than 15 parts of C and obtain an imaginary mixture, represented by a point such as S outside the diagram, containing 42 per cent A, 77 per cent B, and -19 per cent C. Such points may be introduced in the course of a graphical computation, just as negative quantities occur in the course of an algebraic calculation.

129. Polar-coordinate Graph Paper. Another example of special graph paper, which is occasionally useful, is polar-coordinate paper. It has a rather obvious use for the graphical representation of a variable that it is desired to express as a function of an angle. The chart from a recording pyrometer is an example of polar-coordinate paper, the radius representing

temperature, and the angle being marked off in units of time. Figure 83 reproduces some experimental data reported by Drew and Ryan* on the rate of heat dissipation around the perimeter of a 3.19 in. o.d. heated pipe placed in an air stream. The polar distance from the center to the curve represents quantitatively the value of the group hd/k; h is the surface

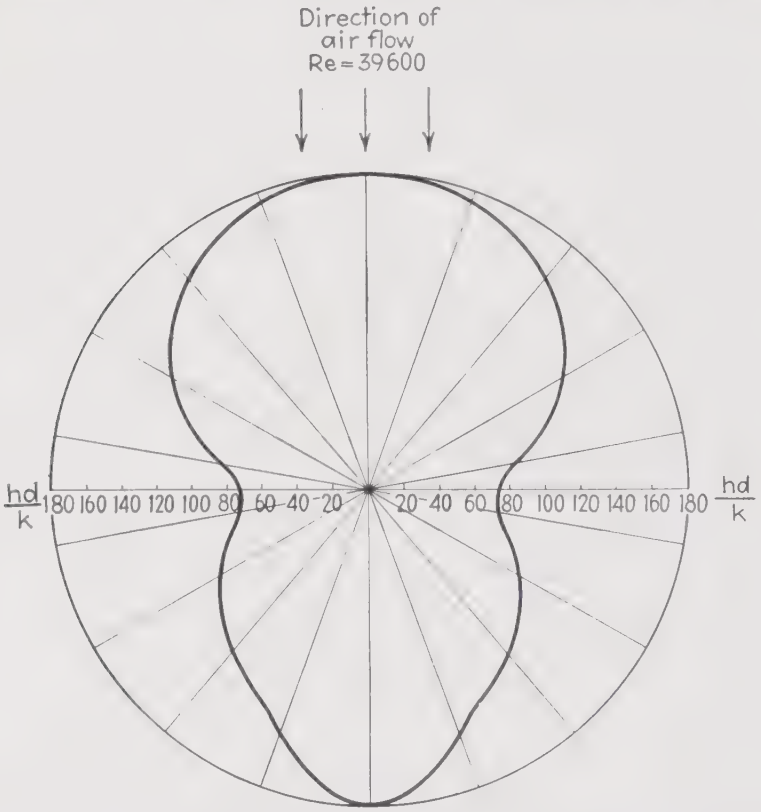

FIG. 83.—Heat loss around perimeter of a pipe in an air stream, expressed in polar coordinates.

coefficient of heat transfer, d is the diameter of the pipe, and k is the thermal conductivity of the air stream. The method of plotting provides an excellent method of visualizing the relative rates of heat loss from different positions around the pipe.

130. Special Types of Graph Paper. The Cox Chart. The practical value of having straight-line representation of data may sometimes justify the preparation of special graph paper to suit the particular function. This is particularly true when

* *Trans. Am. Inst. Chem. Eng.*, **26**, 118 (1931).

a series of values of y in terms of x, each series being for a different value of z, is to be represented graphically. If the nature of the function $y = f(x)$ is similar for each value of z, then a special graph paper prepared to give a straight line for one value of z will give straight lines of y vs. x for the other values of z. A spectacular example of this procedure is the Cox chart of vapor pressures, based on the fact that the curves of vapor pressure vs. temperature represent a similar type of function for most

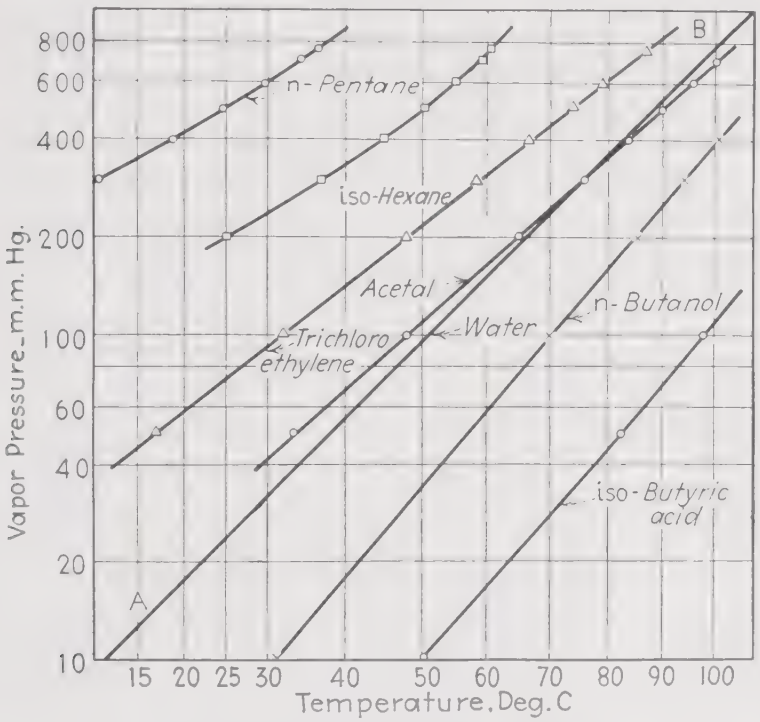

FIG. 84.—Cox chart of vapor pressures.

compounds. If a graph paper is prepared so that the vapor-pressure curve is straight for any one compound, then vapor-pressure data for other compounds will fall on approximately straight lines when plotted on the same graph.

The procedure in preparing such a plot is relatively simple, as illustrated by Fig. 84. One scale is chosen arbitrarily, and the other is laid off in such a way as to make a straight line of the vapor-pressure curve for some compound to be taken as a standard. In this case, a logarithmic scale was arbitrarily chosen for the ordinate (vapor pressure) and the straight line AB drawn in any con-

venient position, but preferably as a diagonal on the graph to be used. Water was chosen as the reference material and a table of vapor pressures for water used in laying off the abscissa scale. For example, the vapor pressure of water at 50°C. is 92.5 mm. The abscissa is marked "50°" at a point immediately below the intersection of the line AB and the horizontal line at the ordinate of 92.5 mm. This process is repeated until the abscissa scale is marked off in as small divisions as may be desired. A special graph paper has thus been prepared on which the vapor-pressure curve of water is, by construction, a straight line. Other vapor-pressure curves of a similar type will also be straight lines, as indicated by the several sample curves shown. The curves for the two hydrocarbons indicate some curvature, and it is roughly true that compounds chemically similar to water will give vapor-pressure curves nearly straight on this graph. If the basis had been benzene instead of water, the curves for pentane and hexane would have been nearly straight, whereas those for butanol and water would have been slightly curved. It so happens that on a Cox chart for the lower hydrocarbons, the curves for the lower straight-chain compounds go through a common point at an extrapolated high temperature. It is also of interest to note that the linear vertical distance between two curves at any fixed temperature represents the difference of the logarithms of the vapor pressures, *i.e.*, the ratio of the vapor pressures. This vertical distance, therefore, represents the relative volatility for those binary mixtures obeying Raoult's law. The curves tend to come together at high temperatures, since the relative volatility decreases with increased temperature.

It should be emphasized that the principle on which the Cox chart is based is general and may find application in many ways. It has been used for plotting viscosity-temperature relations, and special graph paper has been printed for use in plotting viscosity data on lubricating oils. An example of this special paper is given by Marks.*

Specially constructed graph paper may sometimes be used to simplify the calculations when comparing experimental data with a complicated theoretical equation. Figure 85 shows

* "Mechanical Engineers' Handbook," 3d ed., p. 281, McGraw-Hill Book Company, Inc., 1930.

data on temperatures at various points in a thick rubber slab being heated from one face by contact with a hot mold. By comparison of these results with the theoretical equation for unsteady-state heat conduction in a semi-infinite solid, it should be possible to obtain an experimental determination of the thermal diffusivity α (see Chap. VI). One procedure would be to assume various values of α and compare the theoretical and experimental temperature-time curves, obtaining the best value by trial and error. This method would be extremely tedious.

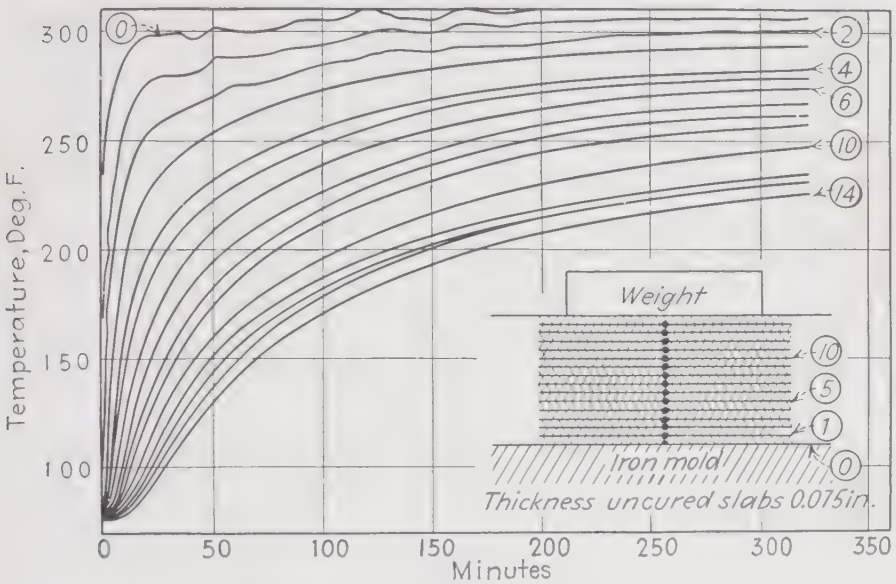

FIG. 85.—Data on temperatures in rubber slab being heated.

The theoretical equation expresses a relation between Δ and τ, where $\Delta = (t - t_0)/(t_1 - t_0)$ and $\tau = \alpha\theta/x^2$. Here t is the temperature at any time θ, t_0 is the mold or surface temperature, t_1 is the initial temperature of the rubber slab, α is the thermal diffusivity $(k/c\rho)$, and x is the distance of the thermocouple from the mold face. Figure 86 is constructed with the ordinate scale so changed as to force the theoretical $\Delta - \tau$ relation to be a straight line. Since the abscissa scale is linear, the theoretical relation between Δ and θ for a constant x and α is also linear and has an intercept at $\Delta = 1.00$. The data replotted in this way on Fig. 86 are seen to give good straight lines. Values of α may be obtained directly by comparison of the geometric slopes of these lines with that of the theoretical $\Delta - \tau$ curve

on the same type of plot or by comparison of values of the abscissa at a constant ordinate. In order that the value of α may be representative of all the data, the slopes may be plotted

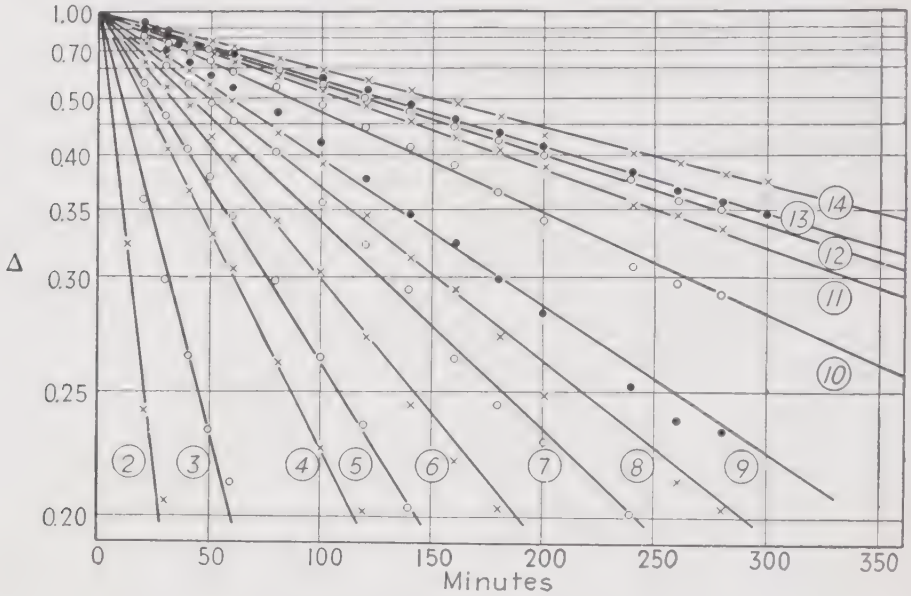

FIG. 86.—Special-ordinate graph.

vs. $(1/x^2)$ and α calculated from the slope of the resulting line. As an alternative, the values of θ at $\Delta = 0.35$ read from Fig. 86 are plotted vs. x^2 in Fig. 87. The failure of the points to fall on a smooth curve is, no doubt, partly due to the displacement of the

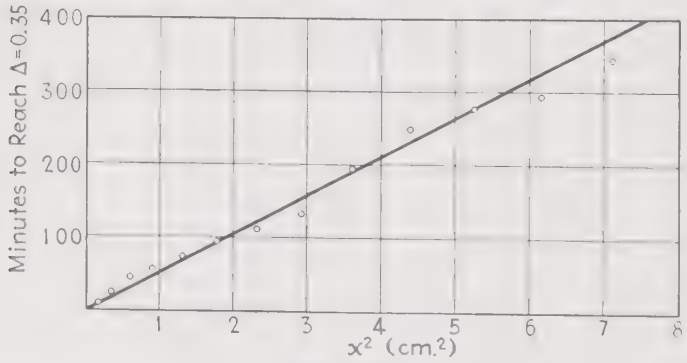

FIG. 87.

thermocouples in the soft rubber being heated, causing an error that is magnified when x is squared. The best line through the points has a slope of 53 min. per sq. cm. Since the theoretical equation gives $\tau = 2.44$ at $\Delta = 0.35$, we have

$$\tau = \frac{\alpha\theta}{x^2} = \alpha \times 53 \times 60 = 2.44$$

and $\alpha = 0.00077$ sq. cm. per sec.

It is evident that the special-ordinate plot has made it possible to replace a tedious trial-and-error calculation by a direct procedure that involves placing best straight lines through plotted points representing the data.

131. Comparison of Data with Theoretical or Empirical Equations. In most experimental investigations, the final step is to compare the data obtained with an empirical equation based on other data or with an existing or proposed theoretical relation. The problem is the reverse of that treated in the preceding chapter, which discussed means of fitting an empirical equation to experimental data. The procedure is similar, and need not be discussed in detail. As in the former case, it is desirable to plot the results in such a way that the theoretical or empirical relation with which they are to be compared will be represented by a straight line, the method of plotting being suggested by the nature of the equation.

In comparing data with theory, it is common for the shape of the curve, but not its position, to be specified by the theoretical equation. This happens frequently when the theory is incomplete and the data are to be used to evaluate certain constants. Under such conditions, it is frequently possible to choose a method of plotting such that the theoretical line through the points should also go through some fixed point, such as the origin, or become asymptotic to some theoretical limit. Additional conditions of this nature imposed by the theory are of great aid in locating the best line through the points. The most elementary example would be a theoretical equation of the form $y = kx$. A few bunched points on a plot of y vs. x might be insufficient to locate the best straight line without the additional condition imposed by the theory that the straight line must pass through the origin.

132. Analysis of Data on Eddy Diffusion. As a typical problem of comparing experimental data with theory, we may refer to the problem of eddy diffusion in a turbulent air stream and consider the data obtained by Towle* on diffusion of carbon

* Massachusetts Institute of Technology, Sc.D. thesis in chemical engineering, 1937.

dioxide. The nature of the experiment will be understood by reference to Fig. 88. Carbon dioxide gas, introduced through an injector tube at the rate of 280 cc. per sec., was released into a continuous stream at the center of a round duct 6 in. (15.24 cm.) in diameter, through which air was flowing at an average velocity

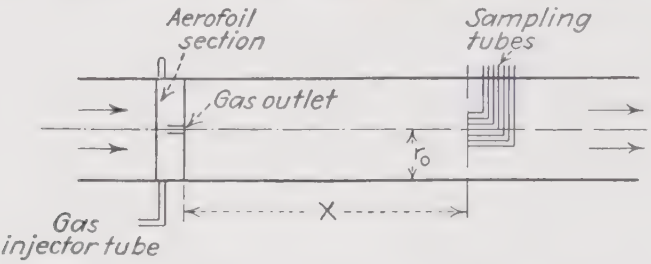

FIG. 88.—Diagram of apparatus for study of eddy diffusion.

of 38.6 ft. per sec. (Re = 119,000). Concentration traverses across the central third of the duct were made at planes 79.7, 112.5, 152.9, 182.1, and 216.4 cm. downstream from the injector tube. The air velocity in the central third of the duct was essentially constant at 49 ft. per sec. (1,490 cm. per sec.). At

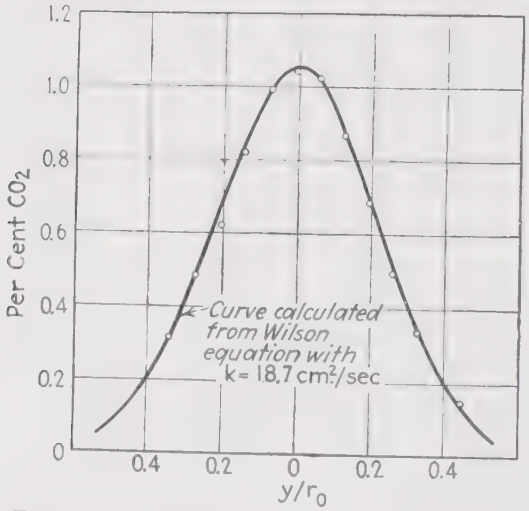

FIG. 89.—CO_2 distribution across air stream.

each sampling plane, samples of gas were removed at a number of points across the diameter and the carbon dioxide content obtained by an accurate volumetric analysis. Figure 89, showing the results of the concentration traverse at a plane 112.5 cm. downstream from the injector tube, is typical of the

results obtained. The abscissa y/r_0 represents the distance of the sampling point from the duct axis, divided by the radius of the duct. Thus $y/r_0 = 0$ at the axis and 1.0 at the wall.

It is desired to employ the data obtained to test the hypothesis that the mixing of carbon dioxide and air in the turbulent stream takes place by a process analogous to molecular diffusion and that the rate of diffusion is proportional to the concentration gradient. The differential equation based on this hypothesis is mathematically identical with the equation derived in Par. 98 [Eq. (18)]. The solution of this differential equation obtained for the present boundary conditions has been given by H. A. Wilson* as

$$C = \frac{q}{4\pi k R} e^{-\frac{V}{2k}(R-x)} \tag{13}$$

where C = concentration of carbon dioxide, volume fraction.
k = diffusion coefficient, or "eddy diffusivity," sq. cm. per sec.
q = rate of injection of carbon dioxide, cc. per sec.
R = distance along a straight line from the injector tube to the point considered, cm.
V = average velocity of fluid stream, cm. per sec.
x = distance along duct axis from injector tube to sampling traverse, cm.
y = radial distance from duct axis to point considered, cm. $= \sqrt{R^2 - x^2}$.

It is desired to find the value of k for which the data would best compare with the theoretical equation. One procedure would be to plot (13) for a number of values of k and so obtain the best value of k by a number of trial calculations. This method would obviously be time consuming and unsatisfactory.

It will be noted that the equation is of an exponential form, easily reducing to

$$\ln CR - \ln \alpha = -\beta(R - x) \tag{14}$$

where

$$\alpha = \frac{q}{4\pi k}; \qquad \text{and} \qquad \beta = \frac{V}{2k}$$

* *Proc. Cambridge Phil. Soc.*, **12**, 406 (1904).

It follows that a graph of CR vs. $(R - x)$ on semilogarithmic coordinate paper should give a straight line having an intercept α and a slope $-\beta$. Figure 90 shows the same data of Fig. 89 replotted in this way. The desired quantity k appears in both α and β and may be obtained independently from the intercept

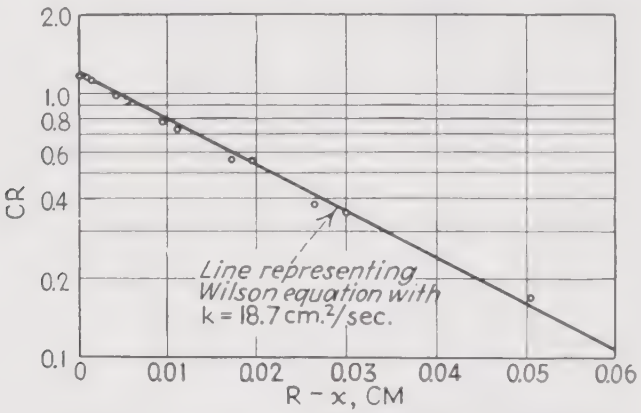

FIG. 90.—Comparison of diffusion data and theory.

at $R - x = 0$ and from the slope of the best straight line through the points. The values of k so obtained are tabulated below.

TABLE XXIII

x (cm.)	79.7	112.5	152.9	182.1	216.4
k_s	15.2	18.8	20.7	21.2	22.5
k_i	14.6	18.6	20.5	22.4	22.8

Values of k obtained from the slope are represented by k_s, and those from the intercept by k_i. As a check on the method of analysis, the solid line on Fig. 89 has been drawn to represent the theoretical equation for a value of k of 18.7 sq. cm. per sec.

Although the values of k_s and k_i agree well, there is a marked increase in both values with increase in x, the distance downstream from the injector tube. By the nature of the analysis, the calculated k represents an average value for the region between injector tube and sampling traverse. If the air flow is disturbed by the injector tube, we may expect that the results at small values of x will not be representative of conditions in normal flow, but the value of k approached asymptotically at large values of x should be that obtainable if no injector tube were present. A graph of k vs. x shows the former to be increas-

ing even at large values of x, and the asymptote can be estimated only approximately, if at all.

Along the axis of the duct, $R = x$, and Eq. (13) reduces to

$$C_0 = \frac{q}{4\pi k x} \tag{15}$$

whence

$$\frac{dC_0}{d(1/x)} = \frac{q}{4\pi k} \tag{16}$$

where C_0 represents the concentration at the axis. If k were a constant, a graph of C_0 vs. $1/x$ would be a straight line. More important, we have obtained a method of plotting whereby the theoretical curve should go through the origin, since C_0

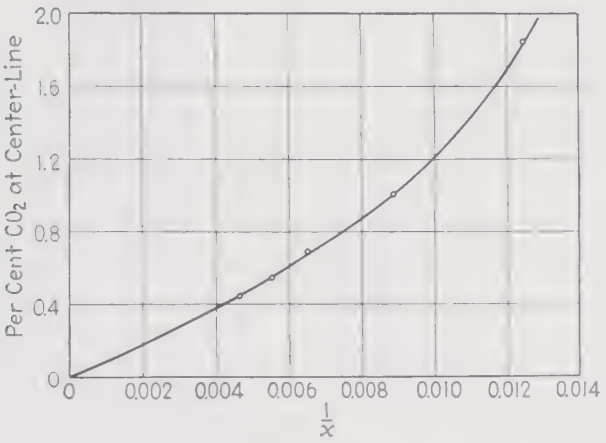

FIG. 91.

approaches zero as x increases indefinitely. The asymptotic value of k should be obtainable from (16) and the measured value of the slope at the origin of a graph of C_0 vs. $1/x$. The data described above have been plotted in this way on Fig. 91, where the values of C_0 are those obtained from the intercepts on semilogarithmic plots similar to those shown in Fig. 90. By extrapolating the curve to the origin and measuring the slope at that point, the asymptotic value of k is obtained as 23.7 sq. cm. per sec.

The picture of eddy diffusion presented is by no means complete, as the process is more complicated than the data discussed above would indicate. Certain of the results of Towle have been selected merely for purposes of illustrating a typical pro-

cedure in comparing experimental data with a theoretical equation.

133. Graphical Aids in Calculations. The use of graphs and alignment charts *solely* as a means of computation is limited, in general, to those cases where the calculation is to be repeated a number of times, and it is therefore economical of time to prepare a graph or chart for the purpose. Exceptions to this rule may be found in those cases where a trial-and-error calculation is involved and a graphical solution is convenient. Graphical means of calculation find wide application, however, in those cases where certain important data involved in the computation are conveniently represented by a graph, and the graphical computation and the graph of the data may be combined. In many cases handled in this way, the computation itself is extremely simple and is carried out graphically only because it involves the use of data best represented by means of a graph.

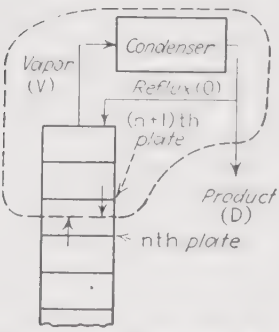

FIG. 92. Upper part of rectifying column.

134. Graphical Design of Rectifying Columns. An important chemical engineering example of combining graphical computation with graphical representation of data is the well-known McCabe-Thiele method for the design of rectifying columns for binary mixtures. Figure 92 represents the upper part of a plate column, showing the condenser and reflux return line. Of the total vapor condensed, D lb. mols are withdrawn as product and O mols returned as reflux to the top plate. The composition of the liquid on any plate (and of the liquid passing to the plate below) is x_n, and the vapor leaving any plate is y_n, both as mol fractions of the more volatile component. A material balance based on the more volatile component for the section indicated by the dotted line is

$$y_n V_n = O_{n+1} x_{n+1} + D x_c$$

and since

$$V_n = O_{n+1} + D$$

then

$$y_n = \frac{O_{n+1}}{O_{n+1} + D} x_{n+1} + \frac{D}{O_{n+1} + D} x_c \qquad (17)$$

where the subscripts refer to the number of the plate on which the streams originate. When the usual assumptions are made that the heat loss from the column is negligible, that the sensible heat required to heat the liquid flowing down the column may be neglected, that the heats of mixing of vapor and liquid streams are negligible, and that the molal latent heat of vaporization is independent of composition, the conclusion is reached that the molal flow of reflux and vapor streams must be constant up and down the column. The subscripts on O may be eliminated in writing (17).

In the ideal column of "perfect" plates, the vapor leaving any plate will have a composition corresponding with the liquid on (and leaving) the plate, and the "plate efficiency" is said to be "100 per cent." In an actual column, this equilibrium may not be reached, but the vapor and liquid compositions are related by the vapor-liquid equilibrium data for the system and by the plate efficiency. If the plates are perfect plates, the vapor composition will be obtained from the equilibrium curve directly.

The general problem with which the engineer must deal is the relation of reflux, number of plates, and degree of separation; *e.g.*, he must determine the number of plates needed to effect a definite separation with a specified reflux. If the liquid and vapor compositions may be calculated from plate to plate, the number of plates required may be found. For the attack on this problem, there are two relations available. Equation (17) gives the relation between the composition of the liquid on any plate and the composition of the vapor rising from the plate next below. The equilibrium diagram (y vs. x) gives the relation between the composition of the liquid on a plate and composition of the vapor rising from the *same* plate. By the alternate use of (17) and of the y-x diagram, the compositions of the liquid and vapor may be calculated up or down the column. The y-x equilibrium data are best expressed by means of a graph. Equation (17) is a linear equation relating y_n to x_{n+1} and is easy to use, but the repeated reference, first to a graph and then to an equation, is tedious and time consuming. McCabe and Thiele* suggested that, since (17) is a linear equation between y and x, it might be represented by a straight line on the same graph used to represent the equilibrium data. The result is indicated by Fig. 93, which

* *Ind. Eng. Chem.*, **17**, 605 (1925).

represents a section of the complete diagram. Starting at any plate n, the liquid composition is obtained from the equilibrium curve AC as y_n. The straight line BD represents (17) and may be used in place of the equation to obtain the composition of the liquid on the plate next above. Passing horizontally from A to B, x_{n+1} is obtained; y_{n+1} is obtained from the equilibrium curve at C, x_{n+2} from the straight line BD, etc. The stepwise construction $ABCD$ serves to designate the vapor and liquid composition for each perfect plate.

The details of applying the method to various design problems need not be discussed, as they are shown in various standard texts as well as in the original article. The method is presented as an excellent example of performing a simple graphical computation in connection with the use of physical or chemical data represented by a graph. In the case of perfect plates, the problem involves only equilibrium data and stoichiometry. The stoichiometric calculation is performed graphically on the equilibrium diagram. Analogous examples in connection with crystallization calculations will be presented later.

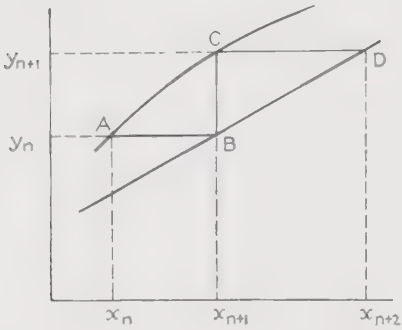

FIG. 93.—McCabe-Thiele diagram.

135. Maximum Capacity of a Filter Press. A common method of operating a filter press is to carry on the filtration at a constant rate until the pressure builds up to the maximum pump pressure and then continue pumping at this constant pressure. The relation between the total volume of filtrate obtained V and time θ is represented graphically by a curve having two branches, one straight and one curved. This is shown by Fig. 94, on which OAB represents a typical relation between V and θ. The straight branch OA represents the constant-rate period, and the branch AB represents the subsequent operation at constant pressure. Such curves may be obtained experimentally or may be calculated, using the standard filtration equations if sufficient basic data on the sludge and press are available.

A practical problem of some importance is the determination of the filtration cycle for which the equipment will give the greatest daily capacity. If the filtering cycle is too short, the time

down for cleaning and reassembling the press will represent too large a fraction of the total time per cycle, and the average rate of filtration will be too small. If the cycle is too long, the average rate will be small because a large part of the filtration will take place with thick filter cakes and proportionately low filtering rates. Assume the relation between V and θ indicated by the curve OAB to have been obtained experimentally or by calculation from known constants in the filtration equations. Let θ_C represent the time for the constant-rate period, θ_P the time for the constant-pressure period, and θ_A the time down for cleaning and reassembling. The over-all average rate of filtration for any cycle will be V divided by $(\theta_C + \theta_P + \theta_A)$. This is

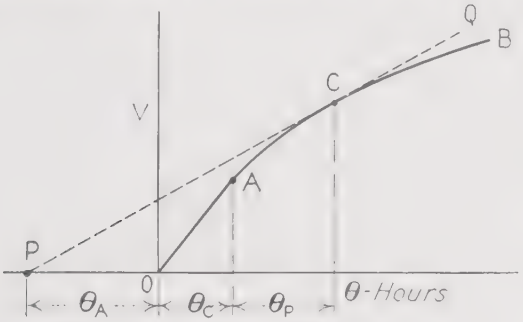

FIG. 94.—Analysis of filtration cycle.

represented by the slope of a straight line PC drawn from P through any point C on the curve, P being placed on an extension of the time axis such that OP represents the time θ_A. The maximum capacity of the press corresponds to the maximum over-all average rate of filtration and is obtained when point C is so chosen that PC will have the maximum slope, *i.e.*, so that PC will be tangent to the curve OAB.

It will be observed that the method is general and that the correctness of the result depends only on the validity of the operating V-θ data. Such data are obtained readily by plant-scale tests, making it unnecessary to rely on theoretical filtration equations. Although constant-rate and constant-pressure periods are included in the cycle described, it is clear that the method is applicable for any type of cycle.

136. Crystallization. Rectangular Coordinates. In the case of the preceding illustrative example, the straightforward numerical determination of the filtration cycle corresponding

to maximum press capacity is not difficult, and the graphical procedure has the advantage only in directness and simplicity. In complicated crystallization problems, a graphical method* is a practical necessity if difficult trial-and-error calculations are to be avoided.

Figure 95 represents a convenient method of representing solubility data for two solutes A and B. The ordinate represents the concentration as lb. A per lb. water and the abscissa as lb. B per lb. water. The curve PQR is the solubility curve for the sys-

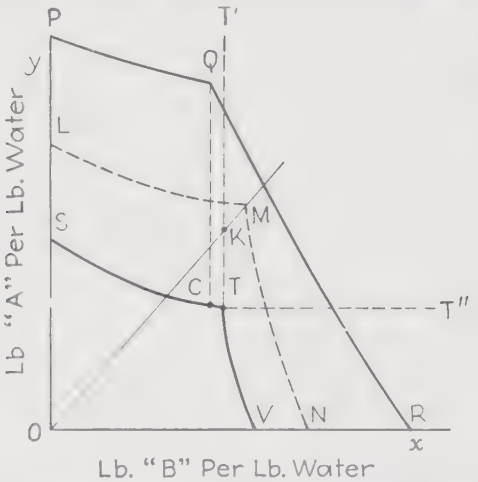

FIG. 95.—Graphical treatment of crystallization stoichiometry.

tem at an elevated temperature t_1, and STV is the corresponding curve for the same system at a lower temperature t_0. Branches PQ and ST represent solutions saturated with A, but not with B, and hence in equilibrium with solid A. Branches QR and TV represent solutions saturated with B, but not with A, and in equilibrium with solid B. Points Q and T represent solutions saturated with both salts and in equilibrium with a crystal mixture of A and B. Any mixture represented by a point above ST will, on cooling to t_0, give crystals of A and a solution represented by a point on ST at the same value of x as at the start. Similarly, mixtures to the right of TV will give crystals of B when cooled to t_0. If the initial mixture is represented by a point above and to the right of T, in the region $T'TT''$ between the two straight dotted lines, then when cooled to t_0 the solution

* See GUGGENHEIM, E. A. and W. H. CAMPBELL, *J. Soc. Chem. Ind.*, **51**, 161T (1932).

will deposit crystals of both A and B, with a mother liquor represented by point T.

If crystals of A and B mixed with some insoluble impurities are leached at t_1, a saturated solution of both salts will be obtained, represented by point Q. If this solution is cooled to t_0, the solution obtained will be indicated by a point C, directly below Q, and the crystals obtained will be pure A. If the solubility relations are such that the curve LMN is obtained at the higher temperature t_1, then, since M is in the region $T'TT''$, cooling to t_0 will result in both crystals being deposited and the mother liquor T will be obtained. In such a case, separation of the two solutes by crystallization is not obtained.

The operations described are based on the assumption that the water content of the mixture remains constant. If water is added, the ratio of A to B is not changed and the ratio of y to x remains constant. The point representing the solution consequently moves toward the origin O on a straight line. If water is evaporated, the point representing the solution moves away from the origin on a straight line through the origin. By adding the proper quantity of water to the saturated solution M, the solution K is obtained. If this is cooled to t_0, only A is precipitated and separation of the two salts is made possible.

The quantities involved are represented on the diagram by distances or may be easily calculated. When the saturated solution Q is cooled to t_0, the weight of A obtained is given numerically by the difference in ordinates Q and C times the total weight of water in the original solution Q. When water is added to M, the new weight of water at K is increased to y_M/y_K times the original weight at M. The weight of crystals obtained on cooling to t_0 is KT times the weight of water at K, or $(y_M/y_K) \times (KT)$ times the original weight of water at M. The water added in going from M to K is obviously

$$\left(\frac{1}{y_K} - \frac{1}{y_M}\right) y_M W_M = \left(\frac{y_M - y_K}{y_K}\right) \times W_M$$

where W_M is the weight of water in the original solution M.

The graphical method is particularly valuable in connection with the crystallization of a double salt. Let W_1 represent the weight of water containing y_1 lb. A per lb. water and x_1 lb. B per lb. water. Assume this solution to be cooled in such a

way as to crystallize a double salt, the composition of which is n lb. A and m lb. B per lb. of water of hydration. The final solution contains W_2 lb. water and has a composition y, x. By material balances,

$$W_1 y_1 = W_2 y + (W_1 - W_2)n$$

and

$$W_1 x_1 = W_2 x + (W_1 - W_2)m$$

whence

$$\frac{y_1 - n}{x_1 - m} = \frac{y - n}{x - m} \tag{18}$$

This is the equation of a straight line through the point x_1, y_1 and the point n, m, representing the composition of the double salt. If double salt is added to the solution x_1, y_1, the composition moves along a straight line toward n, m, whereas if double salt is precipitated the point representing the composition moves away from n, m, on the same straight line.

Figure 96 represents the equilibrium data at 60 and at 15°C. for the system ammonium sulfate–sodium sulfate–water. The curve PQR represents solubilities at 60°, branch PQ being for saturated solutions in equilibrium with solid ammonium sulfate and branch QR for saturated solutions in equilibrium with solid sodium sulfate. Branch LM is for saturated solutions in equilibrium with solid ammonium sulfate at 15°C., but MN represents solutions in equilibrium with the hydrated double salt $(NH_4)_2SO_4$·Na_2SO_4·$4H_2O$. This double salt contains $n = 1.834$ lb. ammonium sulfate per lb. water of hydration and $m = 1.975$ lb. sodium sulfate per lb. water. A saturated solution at Q, on being cooled, will deposit the double salt, and the composition of the mother liquor will follow the straight line QC drawn through Q and a point (not shown) having the coordinates n, m, representing the composition of the double salt. The deposition of double salt on cooling obviously complicates the problem of separating ammonium sulfate and sodium sulfate by fractional crystallization.

One process for separation of the two salts will be described with reference to the diagram. The saturated solution Q is cooled to 15° with the precipitation of the double salt. The crystals are removed and the mother liquor evaporated until x is the same as at the original point Q. The composition moves along CD on a straight line through the origin but eventually

returns to Q, when the evaporation is completed and the solution brought to 60°. During this process, solid ammonium sulfate is precipitated and removed. The solution is held at 60° while both water and double salt are added in amounts exactly equal to the quantities removed during the previous evaporation and crystallization. This may be followed in the two steps QE and EF, with QE a straight line through the origin (addition of water) and EF a straight line through the point n, m, representing

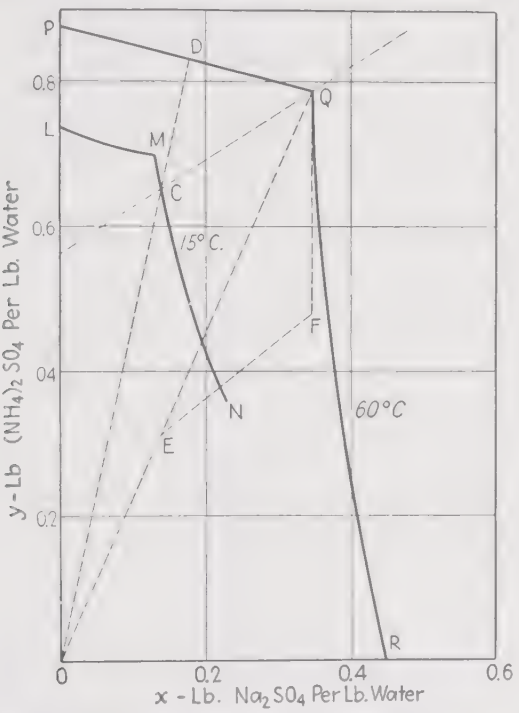

FIG. 96.—Crystallization of hydrated double salt.

the composition of the double salt. Point E is located as having the same abscissa as point C since the ratio of sodium sulfate to water (x) is the same as before the evaporation, precipitation of ammonium sulfate, and addition of water. Point F is located as having the same abscissa as Q, since it is the same solution as Q except that it contains less ammonium sulfate. If a mixture of sodium and ammonium sulphate crystals is now leached at 60°C. with solution F, the original solution Q will be duplicated.

The coordinates of Q are 0.789 and 0.349; hence, 1,000 lb. original solution contain 468 lb. water. The ordinate at F is 0.480, and the amount of ammonium sulfate dissolved in

step FQ is $(0.789 - 0.480) \times 468 = 145$ lb. This is also the weight of the crop obtained in the evaporation process. The weight of double salt precipitated and the weight of water added may be obtained readily from the coordinates of points C or E. It will be noted that the composition of the solution C would be difficult to determine without the aid of a graphical construction.

137. Crystallization. Triangular Coordinates. The graphical treatment of the same problem may be followed by reference to

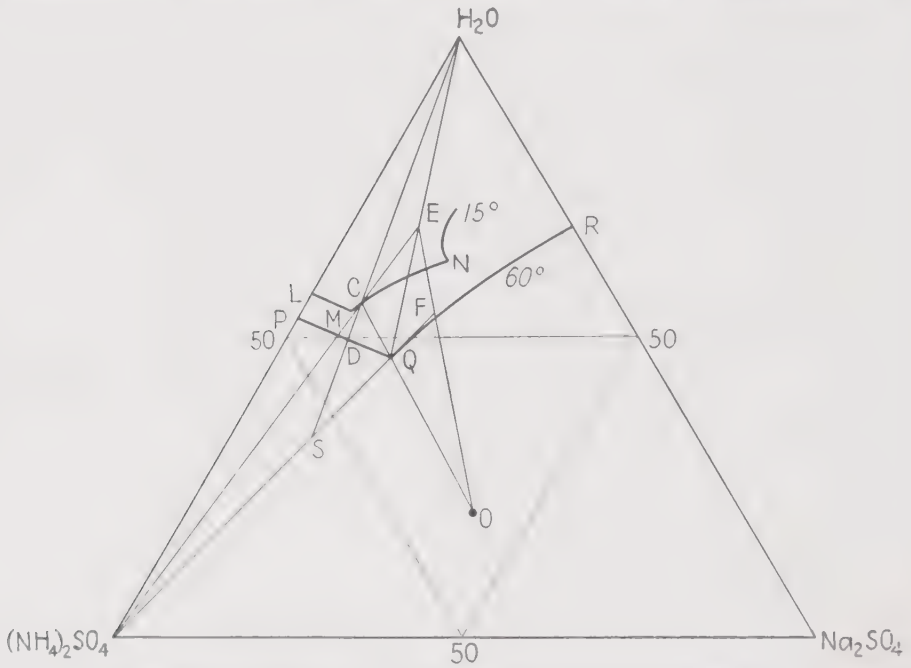

FIG. 97.—Graphical treatment of crystallization employing triangular diagram.

Fig. 97, which is lettered to correspond to Fig. 96. Curves PQR and LMN represent the solubilities at 60° and 15°, respectively. Point O represents the composition of the double salt. From the properties of the triangular graph explained in Par. 128, it is apparent that point C on the 15° curve is obtained by extending a straight line through O and the original solution Q. The double salt is removed, and the evaporation proceeds along CDS on a straight line through the water apex. The corresponding deposition of ammonium sulfate proceeds along SQ on a straight line connecting Q with the ammonium sulfate apex. If we start again at Q, the addition of water is along a straight

line from Q to the water apex, which stops at E at the same sodium sulfate–water ratio as at C (*i.e.*, on a straight line through C and the ammonium sulfate apex). The addition of double salt follows along EO to F, the latter point being on a straight line through Q and the ammonium sulfate apex. The solution of ammonium sulfate in the leaching operation follows the straight line FQ.

The quantities involved may be obtained by employing the rule of mixing brought out in Par. 128. For example, the sum of the mother liquor C and the double salt precipitated in the first step is represented by point Q. The ratio of mother liquor to double salt is represented by the ratio of the length QO to the length CQ, and the ratio of double salt to original solution is the ratio of the length CQ to length CO. The various quantities involved may be obtained by similar ratios, after scaling off the lengths involved. An alternative procedure is to note the coordinates of points C or E and proceed by direct calculation.

The use of triangular graphs for crystallization problems has the advantage that the solubility data in the literature are usually given in a form that may be plotted directly, without preliminary calculations.

138. Enthalpy-concentration Diagrams. Next to the material balance, the so-called "heat balance" is perhaps the most useful tool in chemical engineering calculations. In most cases more properly called an "enthalpy balance," it often requires the use of thermodynamic data, best expressed graphically. Just as the stoichiometric calculations of crystallization may be carried out graphically on the diagram used to express the phase equilibrium data, so the enthalpy balance calculations may be performed graphically on the same diagram employed to represent the thermal data for the system. The enthalpy-concentration graph is sometimes called a "Ponchon* diagram" although Merkel† has done the most in developing its use. McCabe‡ and Thiele§ have described various applications.

The principle of the method may be understood by reference to Fig. 98. Thermal data for a binary mixture are plotted as

* *Tech. moderne*, **13**, 20, 35 (1921).
† *Z. Ver. Deut. Ing.*, **72**, 109 (1928).
‡ *Trans. Am. Inst. Chem. Eng.*, **31**, 129 (1935).
§ *Ind. Eng. Chem.*, **27**, 392 (1935).

enthalpy vs. concentration, with lines of constant pressure or constant temperature or both. In the figure shown, PQ may be assumed to represent the enthalpy of the saturated vapor at a constant total pressure p_0 and RS represents the corresponding enthalpy curve for the saturated liquid at the same pressure. Curve EF is for a subcooled liquid at a constant temperature t_1, obviously having a vapor pressure lower than p_0. The vertical axes represent pure solvent and pure solute, PR being the enthalpy of vaporization of the pure solvent and QS the enthalpy of vaporization of the pure solute. The enthalpy values may be based on any convenient datum state, such as the usual liquid at 32°F. for water, and the datum may be different for solvent and solute. (McCabe uses a very dilute solution at 68°F. as a datum for the solute sodium hydroxide.) When both solvent and solute are volatile, the equilibrium between liquid and vapor phases may be represented by tie lines such as AC, connecting points on the two saturation curves representing the two phases in equilibrium. Although the diagrams are most commonly employed for liquids and vapors, it is apparent that the equilibriums for solid-liquid systems might also be represented in this way, and the graphical method to be described employed for the determination of heat effects in crystallization or leaching.

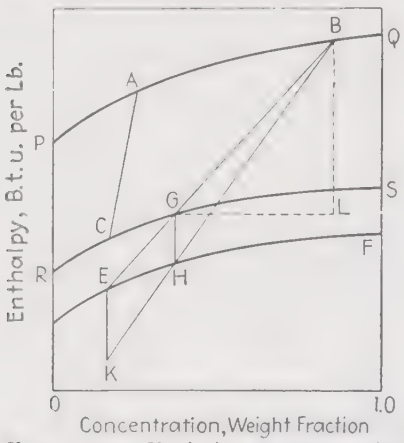

FIG. 98. Enthalpy-concentration diagram.

As in the case of the triangular diagram (Par. 128), it is easily shown that graphs of the type of Fig. 98 lend themselves to the determination of the compositions of mixtures by simple straight-line constructions. Thus, if the saturated vapor B is mixed with the subcooled liquid E, the mixture obtained is represented by some point G on the straight line EB. Moreover, the ratio of the weight of vapor B to the weight of solution E is equal to the ratio of the length EG to the length GB. The weight of vapor B required to be added to the liquid E so as to give a liquid mixture at its boiling point is EG/BG lb. per lb. of liquid E, where G is the intersection of the straight line EB connecting E and B

and the saturated liquid line RS. The heat given up by the vapor is indicated by BL (B.t.u. per lb. vapor) and is seen to be greater than the enthalpy of condensation of B.

If the mixture obtained is to be at the original temperature t_1, then it must be cooled or heat must be evolved as the mixing takes place. The heat evolved is GH B.t.u. per lb. final mixture, since the condition of the latter is represented by point H. Since this condition would be reached by mixing the same quantity of vapor B with the same liquid first cooled to K, the heat evolved may also be taken as the length EK B.t.u. per lb. original liquid E.

If the heat of mixing may be neglected, the calculation of the heat effect is simple, and the graphical procedure has little advantage. If the heat effect is large, the lines of constant temperature for subcooled liquids and the lines of constant pressure for solutions at the boiling point have marked curvature, and the graphical construction is a valuable tool. McCabe* gives numerical examples of the use of such a diagram in the design of a triple-effect evaporator and of a thermocompressor using solutions of sodium hydroxide and water.

139. Absorption Refrigeration. As another example, we may consider the calculation of the important heat quantities in a simple absorption refrigeration machine in which the refrigerant is ammonia and the solvent is water. Merkel and Bosnjakovic† have developed the enthalpy-concentration diagram for this purpose, indicating the construction for various more complicated refrigeration cycles. Figure 99 is a diagrammatic flow sheet of an absorption machine with a heat exchanger but no rectifier. Ammonia is vaporized from the aqueous solution in the still and the vapor condensed in the condenser. The liquid ammonia passes through an expansion valve to the evaporator, where it evaporates at a low temperature and pressure. The vapor formed is absorbed by weak solution in the cooled absorber and pumped back through the heat exchanger to the still. The weak solution from the still returns through the heat exchanger and an expansion valve to the absorber. The still, condenser, and heat exchanger are at the higher pressure p_1; the evaporator

* *Loc. cit.*

† "Diagramme und Tabellen zur Berechnung der Absorptions-Kältemaschinen," Julius Springer, Berlin, 1929.

and absorber operate at a lower pressure p_0. The weak solution has a weight fraction of ammonia C_0; the weight fraction of ammonia in the strong solution is C_1. The exchanger will be assumed to be large enough to preheat the rich solution just to its boiling point at p_1. The pump work will be neglected.

By an energy balance on the whole system, it is obvious that

$$q_S + q_E = q_C + q_A \tag{19}$$

where q_S and q_E are the rates of heat input to still and evaporator and q_C and q_A are the rates of heat output from the condenser

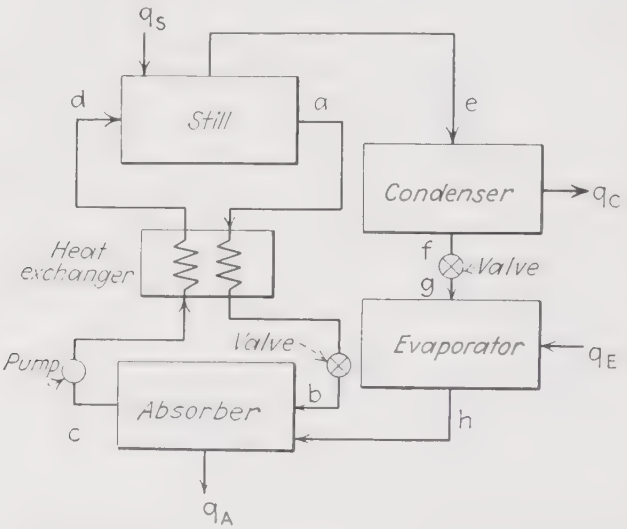

FIG. 99.—Flow sheet of absorption-refrigeration cycle.

and absorber, respectively. Furthermore, if C_2 is the concentration of the vapor leaving the still and R represents the lb. rich solution per lb. vapor, then, by an ammonia balance on the still,

$$RC_1 = C_2 + (R - 1)C_0$$

whence

$$R = \frac{C_2 - C_0}{C_1 - C_0} \tag{20}$$

Figure 100 is a Merkel diagram for ammonia water, with construction lines placed to determine the heat quantities for the absorption cycle described. The weak solution leaving the still at its boiling point is represented by point a at C_0 on the line PQ for saturated solutions at p_1. The vapor leaving the still will

be assumed to be in equilibrium with this weak solution and will be located at the other end of the tie line ac, on the curve Ac for saturated vapor at p_1. The condensation of vapor results in a saturated liquid at p_1 indicated by point f at the abscissa C_2. As the liquid passes through the expansion valve, neither enthalpy nor over-all composition changes, and so points f and g coincide. It must be noted, however, that flashing occurs across this expansion valve, and the resulting mixture of saturated

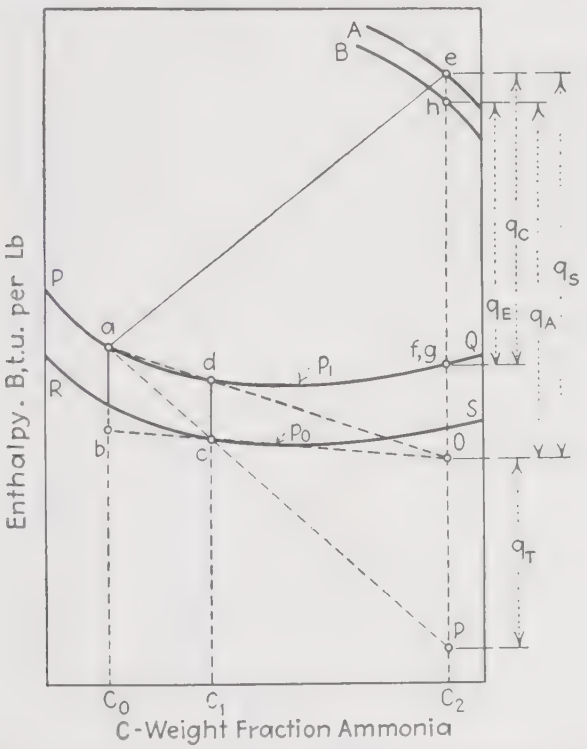

FIG. 100.—Merkel diagram for absorption-refrigeration cycle.

liquid and vapor exists at a pressure p_0 even though its over-all composition and enthalpy remain unchanged. Vaporization in the evaporator produces the vapor h on the saturated vapor line for the low pressure p_0. This is absorbed in the weak solution, which has been cooled from a to some point b in the heat exchanger. The strong solution c produced in the absorber is heated to d in the heat exchanger and delivered to the still. The location of point c on the saturation curve for p_0 assumes that equilibrium is reached in the absorber; point d is on the saturation curve at p_1 because of the assumption that the rich

solution is heated in the heat exchanger just to its boiling point. Depending on the nature of the cycle and of the apparatus, various conditions may be introduced to fix the location of the various points.

The rich solution is heated from c to d in the heat exchanger, and the heat transferred is the length cd B.t.u. per lb. rich solution. The ratio of rich to weak solution is

$$\frac{R}{R-1} = \frac{C_2 - C_0}{C_2 - C_1} \tag{21}$$

When ad is extended to o at the abscissa C_2, point b is located on the extension of oc to the abscissa C_0. By similarity of triangles with apexes at o, it is evident that the ratio of rich to weak solution is the ratio of the length ab to the length cd, whence ab is the enthalpy decrease per lb. weak solution.

The heat transferred in the heat exchanger may also be represented per lb. vapor. When ac is extended to p at C_2, it follows from similar triangles and (20) that

$$\frac{op}{cd} = \frac{C_2 - C_0}{C_1 - C_0} = R$$

and, since cd is the heat exchanged per lb. rich solution, then op is the heat exchanged per lb. vapor generated in the still.

Point o represents a liquid that might be mixed adiabatically with the cool weak solution b to give the rich solution c leaving the absorber. The operation of the absorber may be considered as taking place in two steps: the condensation of the vapor h to give the subcooled liquid o, and the adiabatic mixing of o with b to give c. It is evident that the heat liberated in the absorber is represented by the vertical distance ho B.t.u. per lb. vapor. Similarly, the operation of the still may be considered as taking place in two steps: the adiabatic separation of the rich solution into the two solutions a and o, and the subsequent vaporization of o to form the vapor e. The heat required by the still is represented by the vertical distance eo B.t.u. per lb. vapor.

The important enthalpy quantities are indicated by the vertical lines to the right of the diagram, all representing enthalpy as B.t.u. per lb. vapor. The significant ratio q_E/q_S represents the ratio of refrigeration obtained to heat input to the still.

If no heat exchanger were employed, point d would coincide with c, and a and b would coincide at a. Points o and p would coincide at p, and both q_A and q_S would be increased by the amount q_T, which is the heat transferred by the heat exchanger. It is apparent that any heat transfer accomplished represents a corresponding saving both in heat input to the still and in cooling-water requirements for the absorber. The saving represented by the length q_T is readily visualized by means of the graphical construction.

140. Allowance for Heat of Mixing and Varying Molal Latent Heat of Vaporization in Rectification. The graphical-design method for rectifying columns described briefly in Par. 134 involved several approximations, including the assumptions of no heat of mixing and of molal enthalpies of vaporization independent of composition. The use of the enthalpy-concentration diagram for the graphical computation makes it unnecessary to make these last two assumptions. If Fig. 92 is considered with reference to an enthalpy balance on the section enclosed by the dotted line, it is evident that

$$V_n h_{v,n} - O_{n+1} h_{L,n+1} = D h_{L,c} + Q_c \qquad (22)$$

where V_n represents the mols vapor rising from the nth plate, O_{n+1} is the mols overflow from the $(n + 1)$th plate, D is the mols distillate, $h_{v,n}$ is enthalpy of the saturated vapor leaving the nth plate, $h_{L,n+1}$ is the enthalpy of the boiling liquid leaving the $(n + 1)$th plate, $h_{L,c}$ is the enthalpy of the liquid product, and Q_c is the heat liberated by the condenser. Enthalpy quantities are expressed as B.t.u. per lb. mol of mixture.

Referring to Fig. 101, we see that curve PQ represents saturated vapor and RS liquid at its boiling point at a constant total pressure. The distillate of composition x_c is obtained by condensing the vapor a. If we assume equilibrium between vapor and liquid on each plate, the liquid and vapor compositions are related by the sloping solid tie lines shown drawn in between PQ and RS. The liquid on the top plate is represented by the point b at the other end of the tie line ab. The latent heat of condensation of the vapor rising from the top plate is ap B.t.u. per mol, and the number of mols condensed is $O_c + D$, where O_c represents the mols of liquid returned as reflux. If 1 mol of distillate D is taken as a basis, $h_{L,c}$ is represented by the ordinate of

point p. The quantity Q_c is $(O_c + 1)$ times the latent heat ap, and the right-hand side of (22) is a constant determined by the specified reflux ratio O_c (mols reflux per mol distillate). This constant is represented by point O placed at the abscissa x_c, where $Op = Q_c$, and the ratio Oa/ap is the reflux ratio O_c. It follows from (22) that the composition of the vapor rising from the plate just below the top plate is represented by point c.

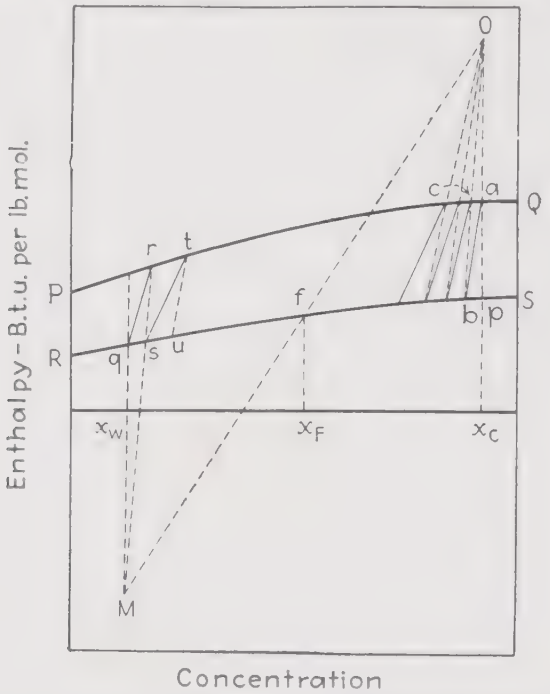

FIG. 101.—Ponchon diagram for rectification calculations.

obtained as the intersection of bO with the vapor line PQ. This is based on the straight-line mixing law, by which (22) is represented by taking c, $(Vh_{v,n})$, as the sum of O (the right-hand side of the equation) and b $(O_{n+1}h_{L,n+1})$. Following down the column, we find that each liquid composition is obtained from the vapor composition by the appropriate tie line, and the vapor composition from the next plate below is obtained by connecting the point O with the point representing the composition of the liquid.

The number of steps needed to reach the liquid composition x_f gives the number of perfect plates required in the rectifying section. Below the feed, the enthalpy balance is

$$O_{n+1}h_{L,n+1} - V_nH_{v,n} = Wh_{L,w} - Q_s = -Q_c - Dh_{L,c} + Fh_F \quad (23)$$

where W is the mols bottoms, $h_{L,w}$ is the enthalpy as B.t.u. per mol bottoms, Q_s is the heat input to the still, F is the mols of feed, and h_F is the enthalpy of the feed. The quantity $Wh_{L,w} - Q_s$ is represented by the point M, obtained by subtracting the constant $Q_c + Dh_{L,c}$ from Fh_F. This relation, obtained by an enthalpy balance on the whole column, is represented diagrammatically by drawing a straight line from O through the feed point f to the bottoms composition x_w. Point q represents the bottoms, and at the other end of the tie line qr is point r representing the vapor leaving the still. As indicated by (23), the liquid on the bottom plate is obtained at s by connecting rM. The vapor leaving the bottom plate is t, the liquid on the second plate is u, etc. The construction is continued up to the feed composition, and the required number of plates in the stripping section is obtained.

Various modifications may be introduced to allow for specified plate efficiencies, etc. For example, if the feed is all vapor, point f will lie on PQ; if the feed is cold, f will lie below RS, but the principal features of the method will be apparent from the simple case described.

141. Triangular Enthalpy-concentration Diagrams. Triangular diagrams have been adapted for use in a number of chemical engineering processes. They have proved to be particularly useful in the treatment of solvent extraction,* and Elgin† has described an ingenious application to the process of leaching. Thormann‡ describes the use of triangular diagrams in the design of rectifying columns for three-component mixtures.

Although triangular graphs find obvious application to ternary mixtures, they may be employed for a variety of other purposes. Walter§ has shown how the Ponchon diagram, such as Fig. 101, may be replaced by a triangular graph in allowing for heats of mixing and variable latent heats when a rectifying column is designed for a binary system. The procedure is analogous to that for extraction, except that enthalpy replaces the solvent as one of the components. A quantity E is defined arbitrarily

* HUNTER, T. G. and A. W. NASH, *J. Soc. Chem. Ind.*, **51**, 95T (1934); T. W. EVANS, *Ind. Eng. Chem.*, **26**, 439 (1934); and K. A. VARTERESSIAN and M. R. FENSKE, *Ind. Eng. Chem.* **29**, 270 (1937).

† *Trans. Am. Inst. Chem. Eng.*, **32**, 451 (1936).

‡ "Distillieren und Rektifizieren," Otto Spamer, Leipzig, 1928.

§ Private communication, 1936.

to represent one "unit" of enthalpy. For example, if E is taken as 7000 B.t.u., then a mixture having an enthalpy of 14,000 B.t.u. per lb. mol is said to contain two equivalents of enthalpy and 1 mol of the binary. The "fraction enthalpy" is then $\frac{2}{3}$, or 0.667. If this mixture contains 50 mol per cent of each component, it is represented by a point on the diagram at the coordinates 0.667, 0.166, 0.166. The usual construction

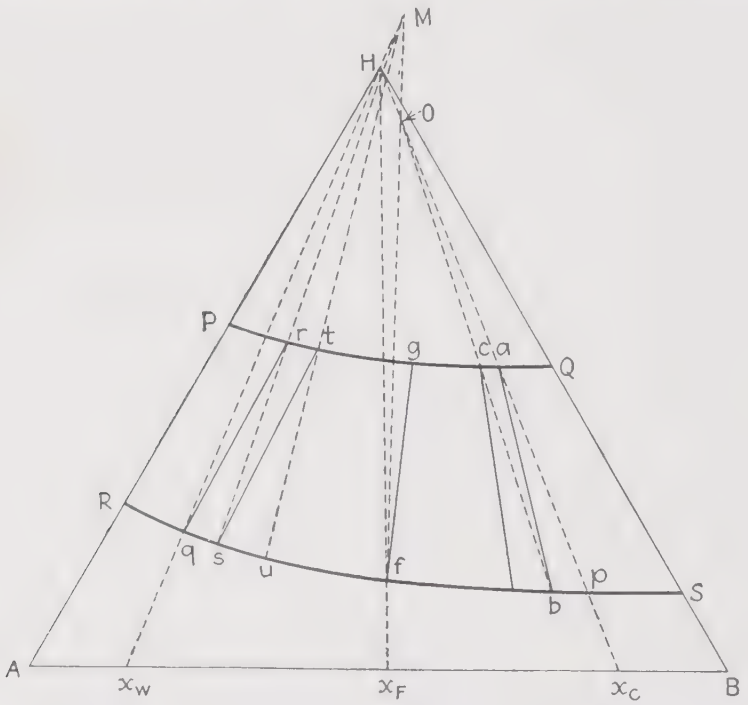

FIG. 102.—Triangular diagram for rectification calculations.

may be employed to carry out the stoichiometric calculations, with points on the diagram representing both quantity and composition of each mixture.

Figure 102 indicates the construction for a binary system in which B is the volatile component. The diagram is lettered to correspond to Fig. 101 to facilitate comparison of the two methods. PQ and RS are the enthalpy curves for the saturated vapor and liquid, respectively. The vertices A and B represent pure components A and B, and H is the enthalpy vertex. Point p represents the distillate at its boiling point; addition of the latent heat of vaporization results in the saturated vapor a, represented by a point at the intersection of pH and PQ. Point

O represents the right-hand side of (22) for 1 mol of distillate. It is located on the straight line through H and x_c at a point such that the ratio of lengths Oa to ap is the reflux ratio O_c, mols reflux per mol distillate. This follows from the properties of the diagram, since

$$(h_{L,c} + Q_c) + O_c h_{L,c} = (O_c + 1)h_{v,t} \tag{24}$$

where $h_{v,t}$ is the enthalpy of the vapor leaving the top plate. The first term, in parentheses, is represented by point O, the second term by point p on the liquid line, and the mixture by point a on the vapor line. The ratio of the quantities mixed is O_c, given by Oa/ap.

The rest of the construction is similar to that of the Ponchon diagram. The liquid on the top plate is obtained at b on the tie line ab; bO gives c representing the vapor from the plate below, etc. The construction point M for the stripping section is obtained as the intersection of fO and qH, where f represents the composition and condition of the feed and q is on the liquid curve at x_w. For total reflux, points O and H coincide; for minimum reflux, point O will lie on an extension of the tie line fq through the feed point f.

Although this method has little advantage over the method of Ponchon, it is an excellent example of the adaptability of the triangular coordinate graph.

142. Alignment Charts. The relation between three variables x, y, and z may be expressed graphically by means of a family of curves on a graph of y vs. x, each curve representing the relation for a fixed value of z. Interpolation between the curves is necessary if the value of z lies between those for which the lines are constructed. An alternative procedure is to represent the relation among the three variables by means of an alignment or nomographic chart, which uses a geometric construction to carry out addition or multiplication. Three scales are laid off along three curved or straight lines in such a way that a straight line will intersect the three lines at values of x, y, and z, satisfying the specified relation between the three variables. The method may be extended to relate any number of variables.

Alignment charts are of value in chemical engineering calculations for three purposes.

1. Calculations that are to be repeated a number of times may be performed quickly and simply by one unfamiliar with the use

of a slide rule or logarithms. For this reason, alignment charts find wide use in plant-control work, as in the case of an operation controlled by the result of a simple titration performed by the operator.

2. In research or design work, it may be found necessary to repeat a time-consuming trial-and-error computation. In such cases, considerable time may be saved by constructing an alignment chart for the purpose, since the use of the chart avoids trial and error.

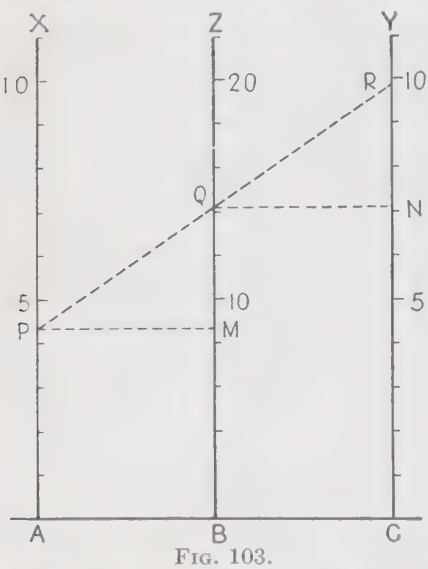

FIG. 103.

3. For design work, it is convenient to have physical and chemical data as well as empirical design data available in the form of alignment charts for rapid estimation of the preliminary design.

A number of alignment charts for chemical engineering use have been published by Chilton, Colburn, Genereaux, and Vernon.* Valuable charts by D. S. Davis and many others have appeared in recent years, including several nomographic humidity charts. In the authors' opinion, however, a number of published charts are worthless because the function represented, or the data on which the chart is based, is not clearly specified.

No attempt will be made to present a thorough outline of the various alignment charts and their construction. It seems desirable, however, to describe one or two of the simpler types in order that the nature of such charts and their possibilities may be understood. Of the various books on the subject, Lipka's "Graphical and Mechanical Computation" (Part I) will be found useful by engineers, although the classical "Traité de Nomographie" by D'Ocagne is the most complete.

A simple alignment chart is shown in Fig. 103. The straight line BZ is midway between the two parallel straight lines AX and CY. The latter are marked off with identical linear scales.

* CHILTON, COLBURN, GENEREAUX, and VERNON. *Trans. A.S.M.E.*, Vol. 55, No. 6, pp. 7–13, May, 1933.

and BZ is marked with a linear scale having divisions just half as large. All three scales originate at the base line AC. The distance AP is px, CR is py, BQ is $\frac{1}{2}\ pz$, where p is a proportionality constant relating distances on the graph to the variables x and y. From the geometry of the figure, it is obvious that

$$2BQ = AP + CR$$

or

$$2(\tfrac{1}{2}pz) = px + py$$

whence

$$z = x + y$$

It follows that any straight line PR will intersect the middle axis at point Q representing a value of z equal to the sum of x and y.

In the somewhat more general case, BZ is not midway between AX and CR, and the scales are not linear. In the preceding example, the equation of the x scale is $AP = px$, *i.e.*, the distance along AX from A is proportional to the value of the variable x. The x scale may be linear in x but marked off with values of any specified function of x. Let the equations of the x, y, and z scales be $AP = pf_1(x)$, $CR = qf_2(y)$, and $BQ = rf_3(z)$. Let the Z axis be placed parallel to AX and CY so that

$$\frac{AB}{BC} = \frac{p}{q} \tag{25}$$

By similar triangles, $RN:QM = QN:PM = q:p$, and

$$\frac{CR - BQ}{BQ - AP} = \frac{q}{p}$$

whence

$$BQ = \frac{pq}{p+q}\left(\frac{AP}{p} + \frac{CR}{q}\right)$$

Now if the z scale is defined so that $r = pq/(p + q)$, then

$$\frac{BQ}{r} = \frac{AP}{p} + \frac{CR}{q}$$

and on substituting the equations of the scales, we have

$$f_3(z) = f_1(x) + f_2(y) \tag{26}$$

It follows that a chart of this type may be used to represent any function of the type (26), provided that the z scale is marked off by the equation

$$BQ = \left(\frac{pq}{p+q}\right) f_3(z) = r f_3(z) \tag{27}$$

and the axes are spaced so that $AB:BC = p:q$. In the case of the above simple example, $p = q = 1$, $r = \frac{1}{2}$, and $f_1(x) = x$, $f_2(y) = y$, $f_3(z) = z$.

The modification necessary to multiply or divide two functions is quite simple. The functions $f_1(x)$, $f_2(y)$, and $f_3(z)$ are written $\log x$, $\log y$, and $\log z$, so that the chart represents the function

$$\log z = \log x + \log y$$

The scales are $p \log x$, $q \log y$, $r \log z$, and, as in the case of Fig. 103, the z axis will fall midway between the other two, if p and q are chosen as equal. The product $z = xy$ is read as the intersection on the z scale of an index line drawn to connect any x and y.

If the equation is $z = x^n y^m$, it may be written in the form

$$\log z = n \log x + m \log y \tag{28}$$

The scale factors p and q are chosen arbitrarily, thus fixing the location of the axes by (25), as in the simple example, but the equation of the x scale is now $AP = pn \log x$, and the y scale is $CR = qm \log y$. The scale factor r is obtained from the relation

$$r = \frac{pq}{p+q} \tag{29}$$

and the equation of the z scale is $BQ = r \log z$. As a simple example of this type of chart, Fig. 104 represents the rate of water flow in a round pipe in terms of the average velocity of the water and the diameter of the pipe. The equation is

$$Q = \frac{\pi}{4} V D^2 \times \frac{60}{144} \times 7.48 = 2.45 V D^2$$

where Q is in gal. per min., V in ft. per sec., and D in in. On the basis of the logarithms,

$$\log Q = \log 2.45 + \log V + 2 \log D$$

First, the length of the scales is decided upon, as, say, 10 in. Next, the ranges of the variables V and D are specified as 0.10

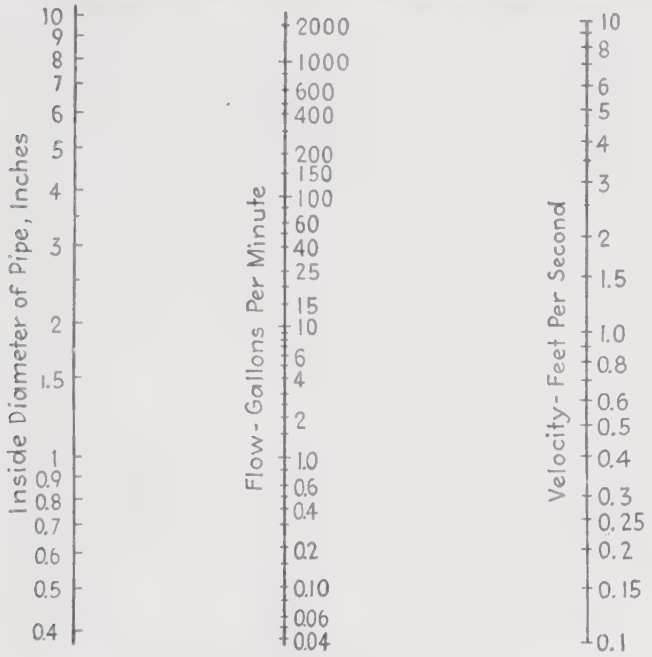

FIG. 104.—Simple alignment chart.

to 10 ft. per sec. and 0.35 to 10 in., respectively. The equation is rewritten

$$\log Q = \log 2.45 + (\log V - \log 0.10) + 2(\log D - \log 0.35) + \log 0.10 + 2 \log 0.35$$

or

$$\log Q - \log 0.030 = (\log V - \log 0.10) + 2(\log D - \log 0.35)$$

which is of the type (26) with $f(z) = f(Q) = \log Q - \log 0.030$, $f(x) = f(D) = 2(\log D - \log 0.35)$, and

$$f(y) = f(V) = \log V - \log 0.10$$

Since the variation in $(\log V - \log 0.10)$ is from 0 to 2, $q = \frac{10}{2} = 5$, and the equation of the y scale is

$$CR = 5(\log V - \log 0.10)$$

Since the variation of $(\log D - \log 0.35)$ is from 0 to 1.456, $p = \dfrac{10}{2 \times 1.456} = 3.43$, and the equation of the x scale is

$AP = 2 \times 3.43$ (log D − log 0.35). This permits the construction of the diameter and the velocity scales as shown in Fig. 104, with $D = 0.35$ and $V = 0.1$ on the same horizontal base line. The z or Q scale is now placed vertically by (27), with $p = 3.43$ and $q = 5$. The value of r is obtained from (29) as 2.03, and the equation of the Q scale is

$$BQ = 2.03(\log Q - \log 0.030)$$

In marking off the latter scale, $Q = 0.030$ is placed at the same horizontal base line as $D = 0.35$ and $V = 0.10$. Another way

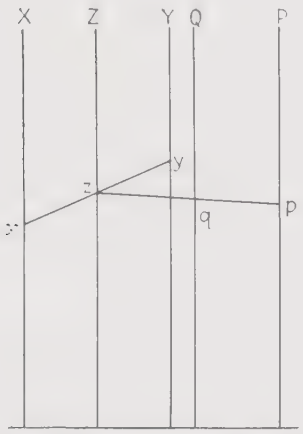

FIG. 105.—Combination of two charts.

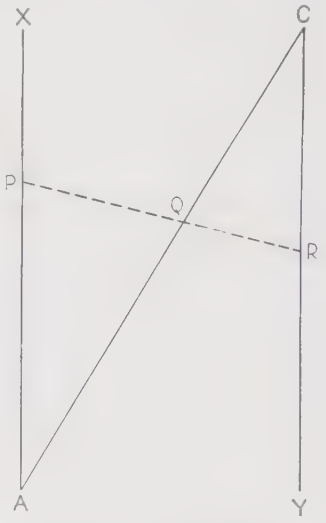

FIG. 106.—Z chart.

to start the Q scale would be to draw the index line from $D = 1.0$ to $V = 1.0$, which must intersect the Q scale at $Q = 2.45$.

The method described represents a graphical procedure for adding any functions of two variables. By the introduction of logarithms, it is not difficult to modify the method in order to multiply or divide two functions. The resulting sum, product, or quotient may be used as the starting point of a second chart, and the addition of three or more functions may be handled in this way. In Fig. 105, the X, Y, and Z axes are drawn so that the index line xy gives the sum $f_3(z) = f_1(x) + f_2(y)$, and the P and Q axes are placed in relation to Z so that an index line zp will cut Q at $f_5(q) = f_4(p) + f_3(z) = f_4(p) + f_1(x) + f_2(y)$. Continuing from Q, other axes may be constructed to provide for still other variables. In order to simplify the chart, the z scale

may be omitted from the Z axis, since it is used for construction purposes only. Furthermore, the Y and Q axes may be combined, with one scale marked on each side of a single line, and P placed accordingly.

The type of chart employing parallel scales accomplishes addition directly and requires the use of logarithmic scales to handle multiplication. An alternative form, illustrated in Fig. 106, accomplishes multiplication directly. The two parallel axes X and Y are connected by the diagonal AC on which the third scale is marked off in the direction AC. By similar triangles, it is evident that

$$\frac{AP}{CR} = \frac{AQ}{QC} = \frac{AQ}{AC - AQ} \tag{30}$$

The equation of the x, y, and z scales is taken as

$$\begin{aligned} AP &= pf_1(x) \\ CR &= qf_2(y) \\ AQ &= rf_3(z) = AC\frac{pf_3(z)}{pf_3(z) + q} \end{aligned} \tag{31}$$

Then by substitution in (30),

$$\frac{CR}{AP} = \frac{qf_2(y)}{pf_1(x)} = \frac{AC}{AQ} - 1 = \frac{pf_3(z) + q}{pf_3(z)} - 1 = \frac{q}{pf_3(z)} \tag{32}$$

whence

$$f_1(x) = f_2(y) \cdot f_3(z)$$

Thus, if the x and y scales are linear and the z scale is marked off in accordance with (31), the index line QR will cut X at a point representing the product of $f_2(y)$ and $f_3(z)$. In the simplest case, $f_2(y) = y$, $f_3(z) = z$, $p = 1$, and $q = 1$, whence

$$AQ = rz = AC\frac{z}{z + 1}$$

The distance AP will then represent the product yz.

If the variables x, y, and z represent logarithms of other variables x', y', z', then the construction may be employed for the equation

$$f_1(\log x') = f_2(\log y') \cdot f_3(\log z')$$

of which a particular example would be

$$\log x' = mn \log y' \cdot \log z'$$

4.1

$$x' = (y')^m(z')^n$$

Many functions of this form are encountered in practice, and this type of alignment chart finds wide application.

As before, the construction may be extended to handle a number of variables. For example, point R may be obtained from an auxiliary chart as the product of two functions, and P will then give the product of three variables. Figure 107 illustrates

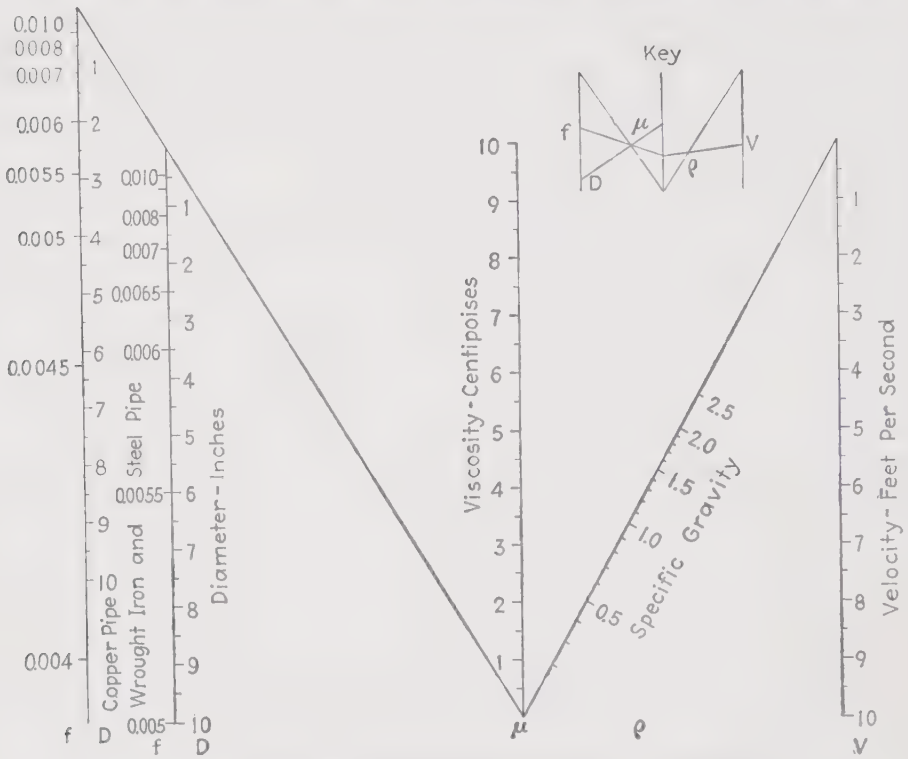

FIG. 107.—Alignment chart for friction factor in fluid flow.

this construction, the Reynolds number being obtained as the product of D, V, ρ, and μ. Instead of the final scale being marked off in numbers representing the Reynolds number, it is labeled with the corresponding values of the friction factor for flow in small round pipes. Two parallel scales are shown for smooth copper and for wrought-iron and steel pipes, the relation between Re and f being obtained from the graph given by Walker, Lewis, McAdams, and Gilliland. This chart illustrates how a function given only by a graph may be introduced into the construction of an alignment chart.

Figure 108 is a chart for the calculation of the heat loss through the wall of an electric oven and is based on the equation

$$q = \frac{\Delta T}{3{,}412\left(1 + \frac{L}{k}\right)} \tag{33}$$

where q is the loss expressed as kw. per sq. ft., ΔT is the temperature difference in °F., L is the oven thickness in in., and k is the thermal conductivity as (B.t.u.) (in.)/(hr.) (sq. ft.)(°F.). The

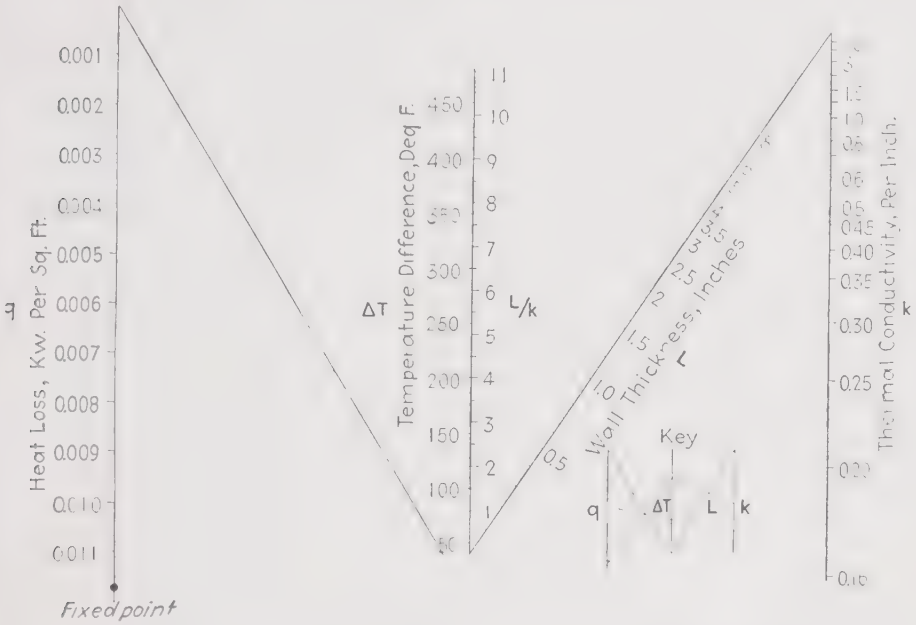

FIG. 108.—Alignment chart for heat loss through oven walls.

surface coefficient is assumed to be 2.0 B.t.u./(hr.) (sq. ft.) (°F.) on both inner and outer surfaces, which accounts for the factor 1.0 to which L/k is added. The right half of the chart serves to multiply L and $1/k$ by the method outlined above. The left-hand diagonal cuts the L/k axis at -1, so that the vertical distance above the intersection is $1 + (L/k)$. This is connected to the fixed point at the lower left, the intersection on the left diagonal connected to the proper ΔT, and this line extended to cut the q scale. An alternative construction would place the ΔT scale at the extreme left with the left diagonal marked as a q scale, thus avoiding the use of the fixed point and eliminating one index line. The construction shown has the advantage

that the final q scale is linear and more easily read. Still another way to construct the same chart would be to place the ΔT scale along the same axis as the k scale, with the q scale along a new diagonal similar to the left diagonal shown, but drawn from the intersection of the k and L scales to a point one unit below the bottom of the (L/k) scale.

The two types of charts that have been described—that with parallel axes and that with one diagonal axis (Z chart)

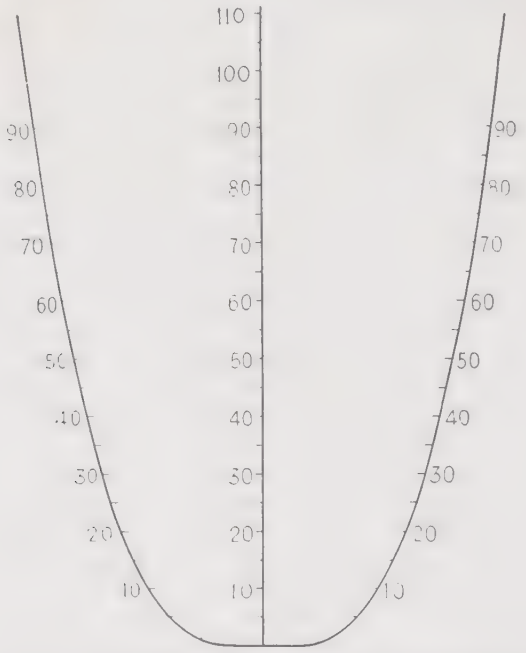

FIG. 109.—Alignment chart for logarithmic mean.

are adequate for the representation of a majority of the functions encountered in practice, although various modifications may be necessary, as illustrated by Figs. 107 and 108. A large number of other charts have been described in the various texts on the subject and are found useful in representing more complicated expressions than can be handled by the two forms described above. One of the commonest of these more complicated charts employs a curved middle axis. Figure 109 is an alignment chart* for determining the logarithmic mean of two quantities and is seen to employ a straight central axis with the two outer axes curved.

* Prepared in 1924 by E. H. M. Lehnhart.

The primary considerations in the preparation of an alignment chart should be its ultimate utility and accuracy. It frequently happens that a workable form may be easily selected but that the resulting chart has various practical disadvantages. One of the most common faults is a widely varying precision in the calculated quantity, depending on the values of the other variables. The precision in obtaining the result may be excellent in one range and very poor in another. In Fig. 107, for example, it is evident that small values of f may be obtained with a precision greater than justified by the data, whereas large values of f may be in error by 10 per cent or more if the chart is small. In such cases, it is necessary to study the various alternative chart forms that can be used to represent the same function, in the hope that one may be found that will avoid such faults.

CHAPTER IX

THEORY OF ERRORS AND PRECISION OF MEASUREMENTS

143. Introduction. The significance of conclusions based upon numerical results is necessarily determined by the reliability of the data and of the methods of calculation in which they are employed. The engineer is, therefore, always concerned with appraisals of reliability, and his appreciation of the principles of error and precision is one of the readiest gauges of his professional competence. Failure to realize the importance of such appraisals not only causes much misdirected effort and expense in both plant and laboratory but may also result in technical blunders and unsound decisions. These statements apply with no less force to the roughest sort of cost estimate than to the most precise determination of physical or chemical constants.

Broadly, the purpose of the material in this chapter might be described in nontechnical terms as "developing a sense of proportion." An elementary example will illustrate the point. Performance tests of a heat exchanger for a proposed installation in a complete process may be made under conditions where the temperature difference at one end of the exchanger is only 2°F., although the proposed operation may involve 20°F. If the thermometers employed in the performance test introduce an error of 1°F. in this 2° difference, the resulting coefficient cannot be highly accurate, even though other data, such as surface areas and rates of flow, are determined with close, but useless, accuracy. As a result, the predictions of how the exchanger will behave when installed will be highly uncertain.

The fundamental principles determining the reliability of numerical results are two in number. (1) The degree of accuracy sought in any investigation should in general depend upon the projected use of the results, and the accuracy of the required data and calculations should be consistent with the desired accuracy in the result. (2) It is desirable to complete the investigation and obtain the required accuracy with a minimum

of time and expense. This second requirement is intimately related to the first, particularly in experimental investigations, because it is usually found that the costs of experiment mount rapidly as the desired degree of accuracy increases. It is most important that the result should be presented in a manner which indicates clearly and logically the limitations on its accuracy and general reliability.

The student or engineer encounters many questions in attempting for the first time to apply the principles that have just been stated in general form. For example, what types of errors are likely to enter into a given measurement or calculation? To what extent do the errors in the data influence the error in the final result? How accurately must the individual quantities entering a calculation be known in order to ensure a specified accuracy in the calculated result? What accuracy is it economically feasible to obtain in a given investigation? The present chapter will attempt to describe the practical techniques that have been developed to answer these questions. Although the general principles and theory to be followed in obtaining these answers are well known, they may, in some cases, particularly in certain engineering problems, be obtained most readily by an appeal to experience. The detailed procedure incident to an estimate of accuracy in any problem will necessarily vary. A discussion undertaken in the evaluation of the accuracy of certain physical or chemical data and involving the methods of least squares would be hopelessly out of place in the estimation of the accuracy of cost calculations on a commercial-size plant designed from pilot-plant data. In either case, however, if the results are to be of value, their accuracy must be investigated.

The engineer seldom makes a rigid study of accuracy but always an approximate one, often subconsciously. In every case, however, judgment is necessary as to the amount of time to be expended in this type of study to guarantee a knowledge of reliability of the results and ensure against obtaining such knowledge by undue effort and expense.

144. Explanation of Terms. The accuracy of a number representing the value of a quantity is the degree of concordance between this number and the number that represents the true value of the quantity; it may be expressed in either absolute or relative terms. This is a qualitative rather than a quanti-

tative definition, and we must become reconciled to the fact that the true value of many quantities can never be known because of unavoidable errors in measurements and calculations. For practical purposes, if X represents the most probable value of a quantity, the absolute accuracy of X may be expressed as $\pm R$, indicating that the true value of the quantity in all probability lies in the range $X \pm R$. This implies that, if another measurement of the quantity were to be made by the same methods, the value obtained, represented by M, would in all probability lie in the range $X \pm R$. An exact terminology would distinguish between M, the value obtained from a single measurement, and the true value of the quantity M_t. A distinction must also be made between the difference $M_t - M$, the error of a measurement, and the difference $X - M$. This latter difference is known as the "residual of a measurement." In conformance with common usage, we shall often refer to the quantity $X - M$ as an "error," although it is really a residual in the sense defined above. For convenience, $\pm R$ may be called the "absolute error" in X, and it is the net effect of all types of errors to which X is subject. The "relative" or "fractional error" in X is $\pm(R/X)$, and the "percentage error" is $\pm 100(R/X)$.

Classification of Errors. All measurements and calculations are subject to two broad classes of errors, *viz.*, determinate and indeterminate errors.

Any error that is discovered and allowed for in magnitude and sign in the form of a correction allowing for its effect is a "determinate error." For example, comparison of an ordinary thermometer with a standard may reveal errors in the graduation of the former and result in a standard calibration. Every temperature measured with this thermometer would then be subject to an error of definite magnitude and sign that could be determined by reference to the standard calibration. Again, an attempt might be made to run an experiment at a certain given value of a quantity. If the quantity varies from this value during the experiment, this variation will be the source of an error. If the manner of variation is known and if it proves possible to calculate the magnitude and sign of the error, a correction may be made and the error is determinate. All errors that either cannot or are not properly allowed for in magnitude and sign are known as "indeterminate errors." It

is obvious that the corrections for determinate errors will themselves be subject to errors and constitute one class of indeterminate errors. In practical investigations, it is very common to encounter errors that might theoretically be determined as to both magnitude and sign by the adoption of a more refined method of measurement and calculation, were this economically justified. Such a situation often arises in preliminary investigations, and here it is essential to make the best possible estimate of the magnitude of the error; such estimated errors are classed as indeterminate. When estimates based upon past experience and best judgment are regarded as inadequate for the purpose at hand, it becomes necessary to devise practicable means for determining the accuracy. For instance, in much engineering work it often proves satisfactory to employ heat and material balances as a basis for indicating probable limitations on the accuracy of a result. Not infrequently, higher standards of accuracy will be necessitated as an investigation progresses, and, with the adoption of more refined methods of measurement, errors that have previously been indeterminate may become determinate.

Accidental Errors of Measurement. A particularly important class of indeterminate errors is that of accidental errors. To illustrate the nature of these, let us consider the very simple and direct measurement of the weight of a crucible by means of an analytical balance. Suppose that several independent weighings are made and that the weight may be read to $\frac{1}{10}$ mg. When the results of the different weighings are compared, it will be found that even though they have been performed very carefully, they may differ from each other by several tenths of a milligram. Experience has shown that such deviations are inevitable in all measurements and that they result from small unavoidable errors of observation due to more or less fortuitous variation in the sensitivity of our measuring instruments and the keenness of our senses of perception. Such errors are due to the combined effect of a large number of undetermined causes and they are known as "accidental errors."

Precision and Constant Errors. The word "precision" is used to denote the extent to which a result is free from accidental errors. It is important to note that *a result may be extremely precise and at the same time highly inaccurate*. For instance, the

weighings just mentioned might all agree to within 1 mg., but from this it would not be permissible to conclude that the weight is accurate to 1 mg. until it can be shown definitely that the combined effects of uncorrected constant errors and the corrections for known errors are negligible compared with 1 mg. It is quite conceivable that the arms of the balance might be of unequal lengths and that the calibration of the metal weights might be grossly incorrect. Such errors as these are constantly present and can never be detected by repeated weighing on the same balance with the same set of metal weights. *Such constant errors can be detected only by performing the measurement with a number of different instruments and, if possible, by several independent methods and observers.* Comparison of the results of such a procedure will in all probability indicate such constant errors if they exist and make them to a large extent determinate. If such a procedure is impractical, the constant errors remain indeterminate and must be estimated. It is not uncommon to find that many plant measurements are highly precise and also highly inaccurate. For example, several samples withdrawn from one point in an apparatus and subjected to analysis might give agreement to a few tenths of 1 per cent indicating high precision, and yet, if these samples should not be representative of the entire contents of the apparatus, the accuracy of their representation of the concentration of the contents of the apparatus might be of such a low order as to render them useless. Errors due to faulty sampling must be guarded against constantly in both plant and laboratory investigations.

Mistakes. A mistake is an error that results from such sources as a faulty record of the observations or a misreading of the indicating instruments or scales. The only safeguard against mistakes is increased care throughout every phase of the investigation. An obvious mistake such as a transposition of digits may often be rectified. Otherwise, the offending observation should be discarded. A mathematical criterion for the rejection of observations is explained in Par. 156.

Errors of Method. These arise as a result of approximations and assumptions made in the theoretical development of an equation used to calculate the desired result and must never be neglected in the estimation of over-all accuracy. For example, the over-all plate efficiency of a rectifying column performing a

given separation is often calculated as the ratio of the theoretical number to the actual number of plates. It is frequently assumed that the over-all efficiency is identical with the individual plate efficiency, but this is an approximation involving an error of method, the extent of which depends upon the location of operating line and equilibrium curve on a McCabe-Thiele diagram. In this case, the error of method might be determined by a more time-consuming calculation, should this be necessary. Unfortunately, many errors of method are indeterminate, and the estimates of their magnitudes can be improved only by lengthy research and investigation. This is usually true of calculations based upon a new theory or hypothesis.

It is also possible for errors to creep into a calculation through errors in the ordinary operations of arithmetic, but, fortunately, these can usually be made negligible by methods to be discussed in the next few paragraphs.

145. Significant Figures. A significant figure is any one of the digits 1, 2, 3, 4, 5, 6, 7, 8, 9, and 0 when it is not used merely to locate the position of the decimal point. For example, the numbers 13,002, 0.32016, 0.000021352, 20.301, and $10{,}905 \times 10^3$ each contain five significant figures. In the number 13,400, there is no way of telling whether or not the two ciphers are significant figures. In such cases, a direct statement of some sort is necessary.

A number is rounded to n significant figures by discarding all digits to the right of the nth place. To round 3.26589 to three, four, and five significant figures, respectively, we write 3.27, 3.266, and 3.2659. In order to round a number with the least possible error, it is convenient to remember the following rules:

1. Increase the digit in the nth place by 1 if the discarded number is greater than half a unit in the nth place.

2. Leave the digit in the nth place unaltered if the discarded number is less than half a unit in the nth place.

3. When the discarded number is exactly half a unit in the nth place, round off so as to leave the nth digit an even number. For example, when rounded to three significant figures, $3.645 = 3.64$, and $3.655 = 3.66$.

This last rule is arbitrary, but the errors due to rounding will tend to be neutralized when it is followed consistently.

Significant Figures and the Numerical Expression of Error. The meaning of absolute and relative error has already been discussed in Par. 144, and it should be clear that, whereas the absolute error of a result depends upon the location of the decimal point, the relative error is dependent solely upon the number of significant figures. It is easy to see that relative error is the more useful index of accuracy of a measurement or calculation. If the volume of liquid withdrawn from a burette is read as 10.25 ± 0.03 cc., this result is less accurate than the volume of liquid in a tank measured as $7{,}500 \pm 15$ gal., inasmuch as the respective relative errors are 1 part in 342 and 1 part in 500. By contrast, the absolute errors in the two cases differ by over a millionfold.

Various rules have been proposed for determining the number of significant figures to be retained in the expression of an error. Any rule adopted in this connection is bound to be arbitrary, but in ordinary work it is fully sufficient to retain only two significant figures in the number expressing an error. The argument for a rule of this nature is illustrated by the following example. Consider the measured volume of liquid,

$$7{,}500 \pm 15 \text{ gal.}$$

The error shows that 7,500 is uncertain by 15 units in its fourth place. One-tenth of this error corresponds to a change of 1.5 units in the fourth place, which is already uncertain by 15 units, and we may elect to consider a change of such magnitude negligible under these conditions. Consequently, a change of equal amount in the error is also negligible, but such a change will always show up as a change of at least one unit in the second significant figure of the error. If it is granted that a change of one unit in the second significant figure of the error is negligible, it must be granted that rejection of all significant figures beyond this place will produce a negligible effect in the number representing the error since the process of rejection produces at most a change of this magnitude. A more tolerant rule would require carrying only one, rather than two, unreliable figures in a result. This latter is customary in engineering work, although the practice must necessarily vary with individual situations.

Once the error in a number is known and expressed to the proper number of significant figures, the number should be

carried out to the place corresponding to the last significant figure of the expression for the error. More significant figures than this will produce a false appearance of accuracy, and fewer will result in a needless sacrifice of accuracy. According to this, we should write, not 15.036 ± 0.15, but 15.04 ± 0.15. The foregoing discussion applies not only to the over-all error of a result but also to the individual errors that go to make up the over-all error.

146. Significant Figures and the Operations of Arithmetic. From the principle that two or, in many cases, only one uncertain figure should be carried in a result, it is possible to formulate certain principles regarding the performance of the ordinary operations of arithmetic.

Addition and Subtraction. When a series of several quantities are added the sum should contain only as many significant figures as the quantity having the greatest absolute error. The error in the sum may possibly be as great as the sum of the absolute errors in the numbers. The sum of the numbers 123, 32.3, 0.276, and 0.0324, each containing one uncertain figure, is 155.6084 if the numbers are added as they stand. Inspection shows, however, that this sum is uncertain in its third significant figure. When rounded to three significant figures, it should be written as 156. This does not have the deceiving appearance of high accuracy suggested by 155.6084.

The operation of subtraction is frequently the source of great loss of accuracy in a calculation in cases where it is necessary to obtain the difference between two large numbers each of which is subject to error. For example, the enthalpy changes in two reactions may be $9{,}654 \pm 40$ cal. and $9{,}435 \pm 50$ cal., respectively. If it is desired to calculate the enthalpy change in a reaction that is the difference between these two, the result is $(9{,}654 \pm 40) - (9{,}435 \pm 50) = 219 \pm 90$ cal. Irrespective of the fact that ± 90 represents the maximum error in the answer and of the argument that the two errors might offset rather than augment each other, one can never be certain of this occurring, and it is clear that two numbers each accurate to less than 0.5 per cent have given rise to a number that is possibly uncertain by over 40 per cent.

All proposed calculations and measurements should be scrutinized carefully for situations of this nature, as their occurrence

frequently necessitates a complete change of method if the desired accuracy is to be obtained.

Multiplication and Division. From Eq. (25), Par. 159, it is seen that the relative error of a product or a quotient may possibly be as great as the sum of the relative errors of the numbers entering into the calculation. Therefore, the result should be given to as many significant figures as are contained in the least accurate number entering the calculation and no more. This is the most conservative practice. However, as will be shown later, there are many cases where the error is probably less than this maximum, and the treatment may be made according to Eq. (51).

147. The Use of Significant Figures in Engineering Calculations and Reports. Although rigid adherence to specific arbitrary rules for the use of significant figures is not essential to good engineering work, it is important to follow the *general principles* that have already been discussed if misleading results are to be avoided. In most instances, the number of justifiable significant figures can be carried on a 10-in. slide rule, and the important exceptions to this procedure will be obvious to one who appreciates the principles of error. Whereas in accurate and precise laboratory work (*e.g.*, certain chemical analytical work) it may be customary to carry two uncertain figures in the result, only one uncertain figure is carried in most engineering work.

Many engineering problems involve economic factors, and the economic data that must enter the calculations are usually of a considerably lower order of accuracy than the technical data. An engineer must be prepared to accept the fact that in many fields where the technical theory and data have reached a point to justify carrying three or even four significant figures in the calculations, economic data such as estimates of operating and investment costs enter the calculations and by their inherent indeterminancy reduce the accuracy of the result to such an extent as to justify its expression by means of only two significant figures. Indeterminate factors of even greater consequence may sometimes be involved in the final decision as to whether a proposed expenditure shall be authorized. The result of technical and economic calculations may be only one factor in a decision involving other factors as diverse as the results of patent litigation and political forecasts.

In the face of these truly indeterminate factors of such great importance, a decision must be made on the basis of business judgment, and under such circumstances it might appear questionable to maintain even ordinary engineering accuracy in the technical calculations. As a general rule, however, it is desirable to maintain as high a standard of accuracy in all calculations and measurements as is possible without undue effort and expense, since this ensures that no unnecessary inaccuracy from the technical results will creep into a decision. Furthermore, experience shows that many calculations and measurements become valuable for purposes entirely unforeseen at the time they were made.

Significant Figures and Financial Accounting Practice. It must be agreed that in the accounting for receipts and disbursements of money, the accounts must be kept accurately down to the smallest unit of money. This may necessitate the use of six, seven, eight, or more significant figures implying a very high order of accuracy. Where balancing of accounts is not involved, however, accounting practice should follow the technical principles of precision of measurements. Practically all cases of estimates by accountants of future performance fall in this category.

148. Independent, Dependent, and Conditioned Measurements. Several measurements on the same or different quantities are independent when

1. No necessary mathematical relation must exist among them.
2. The different measurements are entirely unbiased by each other or by other results.

Measurements that satisfy the second condition, but not the first, are known as "conditioned measurements." Thus, in the complete chemical analysis of a material, a necessary mathematical relation must exist among the percentages of the various constituents inasmuch as these must add up to 100.

Measurements satisfying the first, but not the second condition, are said to be "dependent." It is highly desirable, but often difficult, to avoid dependent measurements. For instance, when a series of readings are being made by resetting the indicator on a scale, if the previous results are remembered, one must contend with the temptation to make the new readings agree closely with the previous results rather than to exercise com-

pletely independent judgment. Such a practice renders it impossible to determine the true precision of the observations since the various readings are not truly independent but are affected by preconceived notions.

149. Direct and Indirect Measurements. All measurements may be classed as either direct or indirect. A direct measurement is made whenever the magnitude of the measured quantity is determined by direct observation from the measuring instrument. The measurement of length by a meter stick, time by a clock, and weight by a balance are all examples of direct measurements. Methods of estimating the magnitude of accidental errors in direct measurements will be considered in the next paragraph.

In contrast to this direct procedure, the magnitude of a quantity is often measured by calculation from the magnitudes of other quantities directly measured, the calculation being made by means of some functional relationship existing among the quantities. The estimate of error in an indirect measurement is more difficult than the estimate of error in a direct measurement since the errors in the direct measurements concerned may either augment or offset each other's effect on the error of the calculated result, depending upon their signs and the form of the functional relationship. Indirect measurements may be made for the purpose of computing a desired quantity from a group of directly measurable quantities by means of a known functional relationship containing known constants or for the purpose of determining the unknown constants in a functional relationship of known form. Methods of estimating the errors in these types of indirect measurements are discussed in Par. 158 and following.

A third type of measurement may be performed for the purpose of determining the form of a functional relationship. Methods by which this may be accomplished have already been discussed in Chap. VII.

150. The Law of Occurrence of Accidental Errors. In many laboratory investigations, it may appear that the only errors of importance are the accidental errors. In any case, one should be familiar with the general methods of treating these errors since they are of importance even when other types of error are involved.

Experience has demonstrated that the occurrence of accidental errors in a series of measurements of the same degree of precision follows three fundamental axioms. In a large number of observations taken on the same quantity

1. Small errors are more frequent than large ones, and the probability of occurrence of an error is a function of its size.

2. Positive and negative errors of the same size are about equal in number.

3. Accidental errors of large magnitude do not occur.

These three axioms, justified by experience, are the basis of the mathematical treatment of errors.

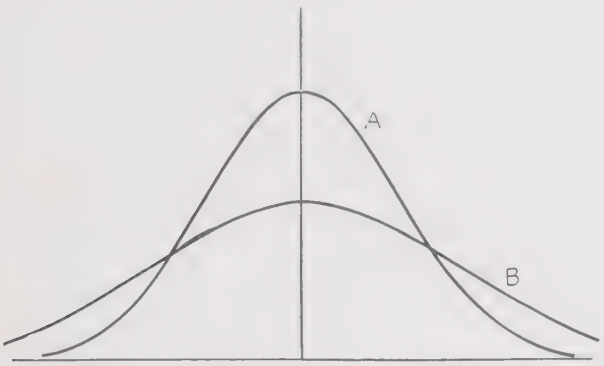

FIG. 110.—Normal-distribution curves.

If a curve of the frequency of occurrence of an error y vs. its magnitude x is constructed (Fig. 110), axiom 2 would indicate that it must be symmetrical about the y axis. Axiom 1 indicates that y must decrease as x increases in either the positive or negative direction, and axiom 3 requires that y become negligibly small at large values of x. An equation satisfying these three conditions is

$$y = ke^{-ax^2} \tag{1}$$

where a and k are constants, and as a matter of fact, this equation may be derived analytically from the three axioms.* It is clear that the probability of occurrence of an error is proportional to its frequency of occurrence in a large number of observations,

*See any good treatise on least squares. For example, D. P. Bartlett, "General Principles of the Method of Least Squares," Massachusetts Institute of Technology, 1900, J. P. Shults, Boston; J. B. Scarborough, "Numerical Mathematical Analysis" The Johns Hopkins Press, Baltimore, 1930.

and it may be shown that, if the area under this curve is taken as unity, the area bounded by the curve, the x axis, and the ordinates at any two values of x is equal to the probability of occurrence of an error between these values of x. The quantity y is called the "error function," and from the fact that the area between the error function and the x axis is taken as unity it may be shown that the constants k and a in (1) are connected by the relation $a = \pi k^2$. If k is placed equal to $h/\sqrt{\pi}$, $a = h^2$ and (1) becomes

$$y = \frac{h}{\sqrt{\pi}} e^{-h^2x^2} \tag{2}$$

often known as the "normal curve of error," normal distribution law, or Gaussian distribution law.

A given series of measurements, each of which is independent, but performed with the same care and by means of the same instruments, will have a given value of h, which is known as the "index of precision" for the series. The smaller the accidental errors of measurement, the higher the precision, and the greater the probability of occurrence of errors of small magnitude. In line with this, Fig. 110 shows the error functions for two different series of measurements. Each series has its own set of errors, the constant h being higher for curve A than for curve B. In a large number of observations, the values of the residuals approach the values of the errors and the error function also represents the distribution of residuals.

151. The Theory of Least Squares. Founded directly upon the three axioms and the resulting normal distribution law is the theory of least squares. Let us imagine making a series of direct observations M_1, M_2 . . . M_n, each of equal precision. Our problem is to employ these observations to determine the most probable value of the measured quantity. If X is taken as this most probable value, the residuals of the individual measurements are $(X - M_1)$, $(X - M_2)$ · · · $(X - M_n)$. These residuals will be denoted by v_1, v_2 . . . v_n. The probability of the separate occurrence of an individual residual is proportional to the value of the error function for this residual, and the probability P that n of the errors chosen together are equal to v_1, v_2 . . . v_n will be proportional to the product of the probabilities of occurrence of the individual residuals, *i.e.*,

$$P = \left(\frac{h}{\sqrt{\pi}}\right)^n (e^{-h^2v_1^2})(e^{-h^2v_2^2}) \cdot \cdot \cdot (e^{-h^2v_n^2})$$

$$= \left(\frac{h}{\sqrt{\pi}}\right)^n e^{-h^2(v_1^2+v_2^2+v_n^2)} \tag{3}$$

The best value to adopt for X will be that value which will give rise to the set of residuals of most probable occurrence. This most probable set of residuals will occur when P is a maximum, and for a given value of h this corresponds to a minimum for the sum $v_1^2 + v_2^2 + \cdot \cdot \cdot v_n^2$. When the definitions of the residuals are substituted, the conditions for a maximum may be expressed as

$$\frac{d}{dX}[(X - M_1)^2 + (X - M_2)^2 \cdot \cdot \cdot + (X - M_n)^2] = 0$$

Carrying out the differentiation, we have

$$(X - M_1) + (X - M_2) \cdot \cdot \cdot + (X - M_n) = 0$$

from which

$$X = \frac{M_1 + M_2 + \cdot \cdot \cdot M_n}{n} \tag{4}$$

an expression recognized as the arithmetic mean of the measurements. Therefore, when the arithmetic mean of a series of measurements of a quantity is taken as the most probable value of the quantity, this ensures that the sum of the squares of the residuals will be a minimum.

152. Weighted Measurements. The concept of a weighted measurement arises from the necessity for a convenient method of comparing measurements of different degrees of precision. A measurement of weight W is defined as one that is equivalent in importance to W measurements of unit weight.

From this definition and an extension of the reasoning in the preceding paragraph, it may be shown that, if h_1 is the index of precision of observations of weight unity and h_2, h_3 . . . h_n are the indices of precision of observations of weights W_2, W_3 . . . W_n,

$$h_2^2 = W_2h_1^2; \qquad h_3^2 = W_3h_1^2; \qquad \text{and} \qquad h_n^2 = W_nh_1^2 \tag{5}$$

When this result and a procedure similar to the one employed for development of (4) are used, it is possible to deduce the

following statement of the most general form of the principle of least squares:

The best value of an unknown quantity that can be obtained from a series of measurements of different precision is that which makes the weighted squares of the residuals a minimum.

This best value is the weighted mean of the measurements and is given by the equation

$$X = \frac{W_1M_1 + W_2M_2 + \cdots W_nM_n}{W_1 + W_2 + W_n} \tag{6}$$

where X is the best, or most probable, value of the quantity and W_n the weight of the individual measurement M_n. Obviously (4) is a special case of (6).

153. Methods of Expressing Accidental Errors. Characteristic Accidental Errors. Several methods are in common use for expressing the magnitude of the accidental error of the most probable value of a quantity determined from a series of measurements. The simplest of these is the mean error.

The Mean Error or Average Deviation. The arithmetic mean of the errors of a series of measurements of equal weight taken without regard to sign is known as the "mean error of a single observation" and may be denoted by e. If the errors are $x_1, x_2 \ldots x_n$,

$$e = \frac{|x_1| + |x_2| \cdots + |x_n|}{n} \tag{7}$$

the notation $|x_1|$ denoting the absolute value of x_1. Since the errors themselves are never known, it becomes necessary to develop a method for approximating the value of the mean error by means of the use of the residuals, which are known. The larger the number of measurements, the more nearly the distribution of residuals corresponds to the normal law; and, when the number of observations n is large, (7) written with the residuals $v_1, v_2 \ldots v_n$ replacing the errors is a good approximation for e. When the number of observations is comparatively small and there is some doubt about the residuals following the normal law, a more accurate formula* for e is

$$e = \text{a.d.} = \frac{|v_1| + |v_2| \cdots + |v_n|}{\sqrt{n(n-1)}} \tag{8}$$

* Space is not available for the complete development of this formula, which, however, may be found in any treatise on least squares.

The mean error, when computed from residuals, is often known as the "average deviation" (abbreviated a.d.). On the assumption that the residuals follow the normal law, it may be shown that the average or probable deviation of a single observation of unit weight is related to the index of precision by the equation

$$\text{a.d.} = \frac{1}{h\sqrt{\pi}} \tag{9}$$

To obtain the average deviation of the mean (denoted by A.D.) we make use of the fact that the mean of a series of n measurements of unit weight has a weight n compared with any observation in the series. Therefore, from Eqs. (5), (8), and (9)

$$\text{A.D.} = \frac{\text{a.d.}}{\sqrt{n}} = \frac{|v_1| + |v_2| \cdots + |v_n|}{n\sqrt{n-1}} \tag{10}$$

Similarly, the average deviation of an observation of weight W_1 is

$$(\text{a.d.})_{W_1} = \frac{\text{a.d.}}{\sqrt{W_1}} \tag{11}$$

In (10) and (11), a.d. refers to a measurement of unit weight and is computed from (8). If the average deviation of measurements of unit weight is to be computed from the residuals of a series of measurements of unequal weights, it is necessary to use the formula*

$$\text{a.d.} = \frac{|v_1|\sqrt{W_1} + |v_2|\sqrt{W_2} \cdots + |v_n|\sqrt{W_n}}{\sqrt{n(n-1)}} \tag{12}$$

Under these circumstances, the formulas for average deviation of a measurement of weight W_1 and average deviation of the mean are

$$(\text{a.d.})_{W_1} = \frac{|v_1|\sqrt{W_1} + |v_2|\sqrt{W_2} \cdots + |v_n|\sqrt{W_n}}{\sqrt{W_1 n(n-1)}} \tag{13}$$

and

$$(\text{A.D.}) = \frac{|v_1|\sqrt{W_1} + |v_2|\sqrt{W_2} \cdots + |v_n|\sqrt{W_n}}{\sqrt{n(n-1)(W_1 + W_2 \cdots + W_n)}} \tag{14}$$

The Probable Error. In addition to the average deviation, there are two other characteristic errors in common use. The

* BARTLETT, *op. cit.*, p. 52.

first of these is known as the "probable error" (p.e.), which is related to a.d. by the equations

$$\left.\begin{aligned} (\text{p.e.}) &= 0.8453(\text{a.d.}) \\ (\text{p.e.})_{w_1} &= 0.8453(\text{a.d.})_{w_1} \\ \text{P.E. (probable error of the mean)} &= 0.8453\ (\text{A.D.}) \end{aligned}\right\} \quad (15)$$

The probable error is in very common use in this country, but its name is misleading inasmuch as it is not the most probable value of the error of a single measurement, as might be implied, but represents an error of such magnitude that from the standpoint of probability the true error of the observation is just as likely to be greater as it is to be less than this magnitude. If the probable error of a quantity M is r, it is quite common to encounter the notation $M \pm r$. This notation for probable error as defined above must not be confused with a similar notation applied to the estimate of over-all accuracy of a result including all types of errors (see Par. 163).

The Mean Square Error. This characteristic error is mentioned here chiefly because it is useful in the derivation of a formula for propagation of errors (see Par. 162). Denoted by μ, its definition in terms of either errors or residuals of measurements of unit weight is

$$\mu = \sqrt{\frac{v_1^2 + v_2^2 \cdot \cdot \cdot + v_n^2}{n}} \quad (16)$$

and is related to a.d. by the formula

$$\mu = 1.2533(\text{a.d.}) \quad (17)$$

The three characteristic accidental errors are proportional to each other, and the formulas of indirect measurements apply to each. In Par. 162, the symbol δ is employed to refer to any one of the characteristic errors. These three errors have interesting geometric interpretations with respect to the normal distribution curve. The quantity μ is the abscissa of the point of inflection, a.d. is the abscissa of the center of gravity, and the ordinate at abscissa equal to p.e. bisects the area under the curve on either side of the y axis.

154. Examples of the Calculation of Characteristic Errors. The following 10 measurements, each of weight unity, refer to a pressure in millimeters of Hg. From these data, compute the most probable value of the pressure, the average deviation of a single measurement, and the average deviation of the mean.

The most probable value of the pressure is given by the arithmetic mean of the 10 measurements and is 64.18. The residuals are listed in the following table:

Measurement..	64.32	64.41	63.96	64.31	64.27	63.78	64.05	64.51	64.38	63.82
Residual.....	+0.14	+0.23	−0.22	+0.13	+0.09	−0.40	−0.13	+0.33	+0.20	−0.36

It is always wise to see whether or not the sum of the positive residuals is equal to the sum of the negative residuals. Although this condition theoretically follows from the use of the arithmetic mean, the sums will be only approximately equal in practice owing to the residuals being rounded numbers.

The average deviation of a single observation of this series is given by (8) and is 0.23. The average deviation of the mean obtained by application of (10) is $0.23/\sqrt{10} = 0.07$.

In another similar series of measurements, how many measurements should be taken to guarantee an A.D. of 0.05? Assuming that a.d. will remain constant at 0.23, we have from (10)

$$n = \left(\frac{0.23}{0.05}\right)^2 = 21$$

This result emphasizes how slowly A.D. decreases after the first few measurements.

Before proceeding to the next example, it will be emphasized once more that these results apply only to accidental errors and indicate nothing with regard to the accuracy of the quantity under discussion. An a.d. of 0.22 indicates merely that if another measurement were to be taken it might be expected on the average to deviate from the mean value by 0.22.

155. The Combination of Sets of Direct Measurements. Several different laboratories were asked to perform the same analysis. The mean of the results reported by each laboratory together with its A.D. appears below.

Laboratory number	Reported percentage	A.D. (percentage)
1	36.42	0.25
2	35.94	0.15
3	37.08	0.10
4	36.67	0.20

If the presence of accidental errors only is assumed, how should these results be combined to obtain the best value and what is the A.D. of this value?

It is necessary to determine first the relative weights of these measurements. By combining (5) and (9), it is seen that the weights are inversely proportional to the squares of the A.D.'s. Assigning a weight of unity to the first measurement, we have

$$w_2 = \left(\frac{0.25}{0.15}\right)^2 = 2.8; \qquad w_3 = \left(\frac{0.25}{0.10}\right)^2 = 6.2; \qquad w_4 = \left(\frac{0.25}{0.20}\right)^2 = 1.6 \quad (18)$$

From these results, it is possible to apply (6) to determine the weighted mean of the measurements.

Denoting the weighted mean by M_0 results in

$$M_0 = \frac{36.42 + 2.8(35.94) + 6.2(37.08) + 1.6(36.67)}{1 + 2.8 + 6.2 + 1.6} = 36.68$$

M_0 is the best value that can be obtained. Since the weight of the first measurement is arbitrarily taken as unity, the A.D. of M_0 is obtained by substitution of A.D. for the first measurement into (11).

$$(\text{A.D.})_{M_0} = \frac{0.25}{\sqrt{1 + 2.8 + 6.2 + 1.6}} = 0.07$$

In problems of this type where it is necessary to determine the A.D. of the best value obtained from the means of several different sets of measurements of different precision, no residuals should be computed, and formula (14) does not apply, because it can take no account of the magnitudes of the given average deviations; it takes account only of their ratios.* Formula (14) may be properly applied to a set of original measurements to which weights have been assigned arbitrarily. When, as in the present problem, it is necessary to combine several different measurements each of which is the mean of a series, the weights of the different measurements may not be arbitrarily assigned but are subject to the relationships indicated by Eqs. (18).

156. Rejection of Doubtful Measurements. When an individual measurement of a series differs widely from the others in the same series, it is possible that the discrepancy may be due to a mistake. The following simple rule is sufficient for most

* SCARBOROUGH, *op. cit.*, p. 328.

ordinary work: omitting the doubtful measurement compute the mean of the series and the average deviation (a.d.) of a single measurement from the mean. Compute the deviation of the doubtful measurement from the mean (*i.e.* the difference between the mean and this measurement); if its deviation is greater than five times the average deviation it should be rejected. This rule rests upon the fact that, granting the normal distribution law, the frequency of occurrence of an observation having a deviation from the mean greater than five times a.d. is less than one in a thousand.

157. Laws of Distribution Other than the Normal Distribution. If a large number of observations of a quantity are made

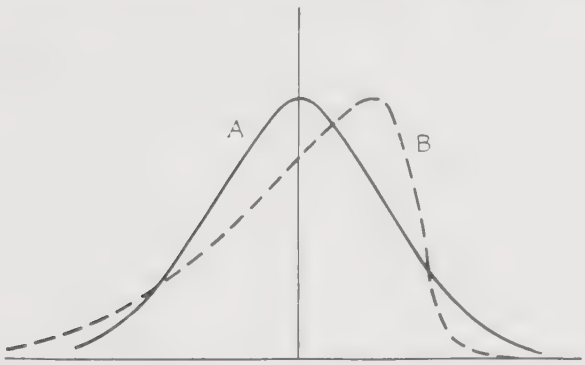

FIG. 111.—Comparison of normal- and abnormal-distribution curves.

and a curve is plotted of the frequency of occurrence of an observed value vs. its magnitude, a curve such as *A* in Fig. 111 will result. Provided that the observations are subject only to accidental errors, experience shows that this curve will be symmetrical about an ordinate erected at the arithmetic mean value of the observations. Curve *A* represents a Gaussian distribution for a series of observations of a given precision, and the most probable or frequently occurring value coincides with the arithmetic mean. In the field of statistics, the most frequently occurring value is called the "modal value."

It is quite conceivable that a series of measurements might result in a distribution such as the dotted curve *B*, Fig. 111. Here it is obvious that the modal value and the arithmetic mean are substantially different. A distribution such as that indicated by curve *B* applies, for example, to the determination of the tensile strength of rubber by means of a large number of

individual tensile tests on the same stock.* The curve indicates a preponderance of "low" values due perhaps to the presence of flaws in the samples. These errors introduced by the flaws are not of the nature of accidental errors. In this case, the most probable value for tensile strength is not given by the arithmetic mean of a series of observations but must be obtained by a system of weighting the observations. If the equation of the distribution curve is known, it is possible to develop formulas for average deviation of a single observation from the modal value, etc., similar to those developed for the Gaussian distribution, which applies only when pure accidental errors are concerned. A great deal of current research is being conducted in the field of statistics to enable one to determine the form of a distribution law from a relatively small number of measurements.

158. The Two Fundamental Problems of Indirect Measurements. When the desired quantity M is related to the several directly measured quantities $M_1, M_2 \ldots M_n$ by the equation

$$M = f(M_1, M_2 \cdots M_n) \tag{19}$$

M becomes an indirectly measured quantity. In general, the true value of M cannot be known because the true values of $M_1, M_2 \ldots M_n$ are unknown, but the most probable value of M, denoted by Q, may be calculated by inserting the most probable values of $M_1, M_2 \ldots M_n$, denoted by $q_1, q_2 \ldots q_n$ into (19). Evidently, the errors in the directly measured quantities will result in an error in the calculated quantity the value of which it is important to know. If the original measurements are available, an obvious method of procedure would be to calculate a value of M corresponding to every set of measurements of $M_1, M_2 \ldots M_n$. The mean of all these calculated values could then be obtained and the characteristic errors of the mean calculated from the residuals.

Very often, however, the only data available are $q_1, q_2 \ldots q_n$ together with their characteristic errors, from which it is necessary to estimate the characteristic errors in Q. It may be that $q_1, q_2 \ldots q_n$ are the most probable values calculated from a set of observations, or they may be merely estimated values employed in the preliminary discussion of the proposed measurement. In these cases, it becomes necessary to devise a procedure

* DAVIES, O. L., and S. HORROBIN, *Rubber Chem. Tech.*, **10**, 180 (1937).

for relating the errors in the measured quantities to the error in the calculated quantity.

Such a procedure makes possible the solution of the two fundamental problems of indirect measurements: *viz.*,

1. Given the errors of several directly measured quantities to calculate the error of any function of these quantities.

2. Given a prescribed error in the quantity to be indirectly measured to specify the allowable errors in the directly measured quantities.

159. Propagation of Errors in a Function of Several Variables. The differential of (19) is by Eq. (22), Par. 74,

$$dQ = \frac{\partial f}{\partial q_1}dq_1 + \frac{\partial f}{\partial q_2}dq_2 \cdot \cdot \cdot + \frac{\partial f}{\partial q_n}dq_n \tag{20}$$

where the q's signify the most probable values of the quantities.

If the differentials dq_1, dq_2 . . . dq_n are replaced by small finite increments Δq_1, Δq_2 . . . Δq_n, there results as a good approximation* for ΔQ the expression

$$\Delta Q = \frac{\partial f}{\partial q_1}\Delta q_1 + \frac{\partial f}{\partial q_2}\Delta q_2 \cdot \cdot \cdot + \frac{\partial f}{\partial q_n}\Delta q_n \tag{21}$$

The quantities Δq_1, Δq_2 . . . Δq_n may be considered as errors in q_1, q_2 . . . q_n, and (21) provides a means for computing the resulting error in the function. Furthermore, (21) holds true for any kind of errors whatever, provided that these are relatively small, and is in no way dependent upon the theory of probability or least squares. The utility of this equation will now be demonstrated by several examples.

* The limitations on this approximation by means of the first differential may become clearer from the following considerations. Errors of Δq_1, Δq_2 . . . Δq_n in the quantities q_1, q_2 . . . q_n will produce a corresponding error ΔQ in Q according to the equation

$$Q + \Delta Q = f(q_1 + \Delta q_1, q_2 + \Delta q_2 \cdot \cdot \cdot q_n + \Delta q_n)$$

Expansion of f in the neighborhood of q_1, q_2 . . . q_n by means of Taylor's theorem gives

$$Q + \Delta Q = f(q_1, q_2 \cdot \cdot \cdot q_n) + \frac{\partial f}{\partial q_1}\Delta q_1 + \frac{\partial f}{\partial q_2}\Delta q_2 \cdot \cdot \cdot + \frac{\partial f}{\partial q_n}\Delta q_n + \frac{\partial^2 f}{\partial q_1^2}\frac{(\Delta q_1)^2}{1 \times 2} + \cdot \cdot \cdot \text{ (terms of higher order)}$$

If the quantities Δq are small, the terms of higher order are negligible and the expression reduces to (21).

Example 1. The average velocity in ft. per sec. of water flowing at 60°F. in a round pipe of cross section A is to be determined by measurement of the weight of water W issuing from the pipe during the time θ, measurement of the pipe diameter D, and calculation from the formula

$$V_{av} = \frac{W}{\theta A \rho} = \frac{4W}{\pi D^2 \theta \rho} \tag{22}$$

Approximate values of the data and the estimated maximum errors are

Variable	Approximate value	Measured to
W	100 lb.	± 1 lb.
θ	70 sec.	± 0.5 sec.
D	1 in.	± 0.01 in.

Estimate the maximum error in the average velocity.

The density of water changes slowly in the neighborhood of 60°F. and is known from the steam tables to be 62.34 lb. $(\text{ft.})^3$. Since this value in order of magnitude is more accurate than the other data, it will introduce negligible error and may be considered constant during the differentiation. Proceeding according to (21), we have

$$\frac{\partial V_{av}}{\partial W} = \frac{4}{\theta \pi D^2 \rho}; \qquad \frac{\partial V_{av}}{\partial \theta} = -\frac{4W}{\pi D^2 \rho \theta^2}; \qquad \frac{\partial V_{av}}{\partial D} = -\frac{8W}{\theta \pi \rho D^3}$$

and

$$\begin{aligned} \Delta V &= \frac{4}{\theta \pi D^2 \rho}\Delta W - \frac{4W}{\pi D^2 \rho \theta^2}\Delta\theta - \frac{8W}{\theta \pi \rho D^3}\Delta D \\ &= \left[\frac{(4)(144)}{70(3.14)(1)(62.3)}\right]\Delta W - \left[\frac{4(100)(144)}{(3.14)(1)(62.3)(70)^2}\right]\Delta\theta - \\ &\qquad \left[\frac{8(100)(1728)}{(70)(3.14)(62.3)(1)}\right]\Delta D \\ &= 0.042\Delta W - 0.060\Delta\theta - 100\Delta D \end{aligned} \tag{23}$$

In order to obtain the maximum error, the sign of the ΔW will be taken as positive and the signs of ΔQ and ΔD will be taken negative. Therefore,

$$\Delta V_{max} = 0.042(1) + 0.060(0.5) + 100\left(\frac{0.01}{12}\right) = 0.042 + 0.030 + 0.084 = 0.156 \text{ ft./sec.}$$

Since the approximate value of the velocity is

$$V = \frac{(4)(100)(144)}{70(3.14)(1)(62.3)} = 4.21 \text{ ft. per sec.}$$

the maximum percentage error is $\pm(0.156\ 4.\ 21)100 = \pm 3.7$ per cent

A question may now be raised as to the necessity of solving the preceding example by the use of (20). An obvious method of estimating the maximum error would be to make two calculations with (22): (1) inserting the approximate values of the various quantities, and (2) increasing or decreasing these quantities by an amount equal to the error of measurement and repeating the calculation. The difference in the two results represents the maximum error.

$$\Delta V_{\max} = (V + \Delta V)_{\max} - V = \frac{4(144)}{\pi\rho}\left(\frac{101}{69.5(0.99)^2} - \frac{100}{70(1)^2}\right)$$

There is nothing wrong theoretically with this procedure, but inspection shows that this calculation necessitates taking the difference between two numbers that are near each other in value and, though it can be performed with sufficient accuracy in the present case, it is evident that as the errors become smaller more significant figures must be carried to obtain the same degree of accuracy. This difficulty is not encountered when (21) is used. Another reason for the introduction of (21) lies in its great utility in connection with the problem of estimating allowable errors in the individual measurements for a prescribed error in the calculated result.

Several points of importance may be noted from this example. First of all, it will be seen that the error in a calculated quantity that is a function of several directly measured quantities depends on (1) the nature of the function, (2) the magnitudes of the measured quantities, and (3) the magnitudes of the errors. In the second place, variables such as ρ, whose values are known much more accurately than the rest of the variables, may be considered constants during the differentiation, since the error they introduce into the final result will be negligible. In the third place, it is clear that the actual error in V might not equal the maximum error calculated, since errors in the various measured quantities might offset each other. If it is assumed

that all types of errors excepting accidental errors are negligible and that the magnitudes of these errors as reported above have been determined by calculation from data from several independent runs, it is valid to apply a formula which allows for the fact that in the most probable case the various errors will to a certain extent offset each other (see Par. 162).

In the fourth place, it should be pointed out that in the case of formulas of the type of (22) consisting of the products of powers of the variables it is possible to effect a simplification in the calculations by the use of fractional errors. To illustrate this, consider the general function

$$Q = (q_a^a)(q_b^b) \cdot \cdot \cdot (q_n^n) \tag{24}$$

Applying (21) gives

$$\Delta Q = (q_b^b \cdot \cdot \cdot q_n^n) a q_a^{a-1} \Delta q_a + (q_a^a q_c^c \cdot \cdot \cdot q_n^n) b q^{b-1} \Delta q_b \cdot \cdot \cdot$$

and

$$\frac{\Delta Q}{Q} = a\frac{\Delta q_a}{q_a} + b\frac{\Delta q_b}{q_b} \cdot \cdot \cdot + n\frac{\Delta q_n}{q_n} \tag{25}$$

which states that the fractional error in the function Q is given by the sum of the fractional errors in the measured quantities each multiplied by the respective power to which it appears in the function. When (25) is multiplied by 100, it is seen that the same rule applies to percentage errors. This rule provides a rapid solution of the preceding example. The percentage errors in W, θ, and D are 1, 0.7, and 1 per cent, respectively. W enters to the first power, θ to the negative first power, and D to the minus second power. The maximum percentage error is then obtained when the percentage errors in D and θ are taken negative and the percentage error in W taken positive, or vice versa. Equation (25) gives

$$(\Delta V_{av}/V_{av})100 = 1\% + 0.7\% + 2(1\%) = 3.7\%$$

(either plus or minus) which checks satisfactorily the result from (23).

Example 2. It is suggested that an attempt be made to measure V_{av} in (22) to within an error of $\pm 2.0\%$. Under this condition, what are the maximum allowable errors in the directly measured quantities W, θ, and D?

Either (21) or (25) may be used, but it is apparent that there is no unique answer to the problem as stated. More conditions are necessary. For example, the value of two errors might be fixed, whereupon the value of the third is fixed. In this general type of problem, it must be recognized that the labor and expense involved in measuring the various quantities to a given degree of accuracy are different. Ideally, those quantities which are easiest to measure should be measured the most accurately, more tolerance being allowed in the more difficult measurements so that the required accuracy in the final result will be obtained with a minimum of expense for labor and apparatus. Because there is no general relationship between the difficulty and the accuracy of measurements, this condition cannot be given exact mathematical expression. As a starting point, it is customary to impose the condition that the errors in each of the directly measured quantities contribute equally to the error in the function. This condition is known as the "principle of equal effects."

Applied to (21) with the understanding that the sign of each Δq will be taken such as to make all terms of the same sign and will result in the maximum error in ΔQ, the principle of equal effects gives

$$\Delta Q = n\frac{\partial f}{\partial q_1}\Delta q_1 = n\frac{\partial f}{\partial q_2}\Delta q_2 = \cdots n\frac{\partial f}{\partial q_n}\Delta q_n \tag{26}$$

In the case of a function such as (24), it is convenient to work with fractional errors, and the principle of equal effects reduces (25) to

$$\frac{\Delta Q}{Q} = na\frac{\Delta q_a}{q_a} = nb\frac{\Delta q_b}{q_b}, \text{ etc.} \tag{27}$$

Employing (27) in the solution of Example 2, we have in the case of W

$$100\frac{\Delta V}{V} = 2.0 = 3(1)\frac{\Delta W}{W}100$$

from which $100(\Delta W/W) = 0.7$ or ± 0.7 lb. per 100 lb. Similar calculations for the allowable errors in θ and D give ± 0.5 sec. and ± 0.003 in., respectively. These results should not be considered inflexible but should serve as a basis for deciding the optimum errors to tolerate in each quantity to ensure an error of no more than 2 per cent in the calculated velocity with minimum labor and apparatus. Discussions of the kind illus-

trated by the two preceding examples often serve to reveal that some quantity is being measured with a higher degree of precision than necessary, in view of the magnitude of the errors inherent in the other quantities concerned, or that particular attention must be focused upon the accurate measurement of a certain quantity owing to its unusually large influence on the final calculated result. Unfortunately, in many important cases the functions are quite complex, and calculations involving data known only in the form of tables and curves are necessary. The estimation of errors in such cases is more difficult and not infrequently can be accomplished only by actual repetition of the calculations and comparison of the results obtained from different sets of values of the measured quantities.

160. Evaluation of Errors in More Complex Expressions. An example of the treatment of a more complicated type formula occurs in the discussion of the measurement of a heat-transfer coefficient. The over-all coefficient of heat transfer of a shell-and-tube water heater is to be determined from measurements of steam pressure, terminal water temperatures, and rate of flow of the condensate formed. The over-all coefficient U for the entire heater is *defined* by the equation

$$q = UA\Delta_m \tag{28}$$

where q = rate of heat transfer, B.t.u. per hr.

A = area of heater, sq. ft.

Δ_m = log mean-temperature difference $= \dfrac{(\Delta_1 - \Delta_2)}{\left(\ln \dfrac{\Delta_1}{\Delta_2}\right)}$.

U = over-all coefficient, B.t.u./(hr.)(sq. ft.)(°F.).

It is desired to know what accuracy is required in the individual measurements if the coefficient is to be accurate to 5 per cent. The circumstances are such that it is possible to make only one run. Approximate values of the data are

Steam pressure	2 lb. per sq. in. (gauge)
Heating surface	100 sq. ft.
Condensate rate	2,500 lb. per hr.
Condensate temperature	216°F.
Inlet-water temperature	50°F.
Discharge-water temperature	160°F.

The saturation temperature for steam condensing at 16.7 lb. per sq. in. abs. is known from the steam tables to be 219°F

It will be assumed that the amount of inert gas present is negligible and that the steam condenses at a temperature corresponding to the measured pressure. Figure 112 is a schematic diagram of distance through the exchanger vs. temperature on both steam and water sides. The amount of heat transferred by the condensate dropping from 219 to 216°F. is slight compared with the total heat transferred and will be neglected.

It is recognized that the over-all coefficient at any point varies somewhat throughout the heater owing to a variation in the water-film coefficient, but this variation is not great and does

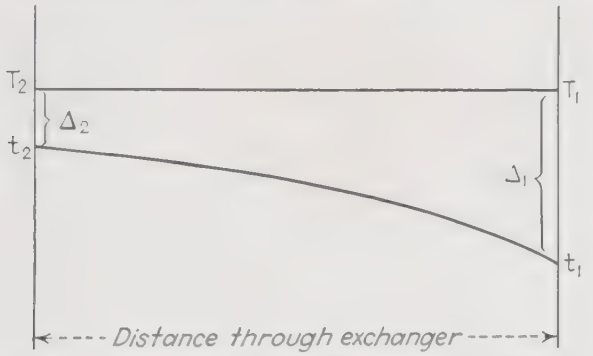

FIG. 112.—Temperature distribution in heat exchanger.

not invalidate the use of the log mean-temperature difference in (28), which is merely a definition of U for the present case.

When (28) is written in the form

$$U = \frac{q}{A\Delta_m}$$

it is seen that (25) is applicable and

$$\frac{\Delta U}{U} = \frac{\Delta q}{q} - \frac{\Delta A}{A} - \frac{\Delta(\Delta_m)}{\Delta_m} \tag{29}$$

The permissible percentage error in each of q, A, and Δ_m for an error of 5 per cent in U is $(\frac{5}{3})\% = 1.67\%$. In the case of A, this amounts to 1.7 sq. ft. The over-all rate of heat transfer q is given by the product of the condensate rate and the latent heat of condensation of the steam. The latter can be determined very accurately from the steam tables, but the value selected will depend upon the pressure. The allowable error in the pressure measurement will be a function of the allowable error in the temperature measurements. Therefore the calculation

of allowable error in the condensate rate had best be postponed until after a discussion of the temperature measurement.

With reference to Fig. 112, Δ_m is defined by the equation

$$\Delta_m = \frac{\Delta_1 - \Delta_2}{\ln \frac{\Delta_1}{\Delta_2}} \tag{30}$$

and it is important to note that the numerator and denominator of this expression are not independent. An increase in Δ_1 in the numerator, for example, is partly offset by the same increase in Δ_1 in the denominator. There are several methods of proceeding from this point, but perhaps it is easiest to compute the allowable error in Δ_m.

$$\Delta_m = \frac{(219 - 50) - (219 - 160)}{2.3 \log \frac{219 - 50}{219 - 160}} = \frac{110}{1.05} = 105°\text{F.}$$

The allowable error then becomes

$$(0.0166)(105) = \pm 1.74°\text{F.} = \Delta(\Delta_m)$$

Applying (21) to (30) results in

$$\Delta(\Delta_m) = \frac{\left[\ln \frac{\Delta_1}{\Delta_2} - (\Delta_1 - \Delta_2)\frac{\Delta_2}{\Delta_1}\frac{1}{\Delta_2}\right]\Delta(\Delta_1)}{\left(\ln \frac{\Delta_1}{\Delta_2}\right)^2} + \frac{\left[-\ln \frac{\Delta_1}{\Delta_2} + (\Delta_1 - \Delta_2)\frac{\Delta_2}{\Delta_1}\frac{\Delta_1}{\Delta_2^2}\right]\Delta(\Delta_2)}{\left(\ln \frac{\Delta_1}{\Delta_2}\right)^2} \tag{31}$$

By the principle of equal effects

$$\Delta(\Delta_1) = \frac{\Delta(\Delta_m)\left(\ln \frac{\Delta_1}{\Delta_2}\right)^2}{2\left[\ln \frac{\Delta_1}{\Delta_2} - \left(1 - \frac{\Delta_2}{\Delta_1}\right)\right]} = \frac{1.74(1.05)^2}{2[1.05 - (1 - 0.35)]} =$$

$$\pm 2.4°\text{F.} \tag{32}$$

$$\Delta(\Delta_2) = \frac{\Delta(\Delta_m)\left(\ln \frac{\Delta_1}{\Delta_2}\right)^2}{2\left[\ln \frac{\Delta_1}{\Delta_2} + \left(\frac{\Delta_1}{\Delta_2} - 1\right)\right]} = \frac{1.74(1.05)^2}{2[-1.05 + (2.86 - 1)]} =$$

$$\pm 1.2°\text{F.} \tag{33}$$

but $\Delta_1 = (T_1 - t_1)$ from which $\Delta(\Delta_1) = \Delta T_1 - \Delta t_1$, and by the principle of equal effects

$$\Delta T_1 = \Delta t_1 = \pm\frac{2.4}{2} = \pm 1.2°\text{F.}$$

Similarly, $\Delta_2 = (T_2 - t_2)$, from which $\Delta(\Delta_2) = \Delta T_2 - \Delta t_2$; and by the principle of equal effects

$$\Delta T_2 = \Delta t_2 = \pm\frac{1.2}{2} = \pm 0.6°\text{F.}$$

At 219°F., an error of 1°F. corresponds to an error of 0.3 lb. per sq. in. in the pressure. Therefore, the pressure must be measured to $(0.6)(0.3) = \pm 0.2$ lb per sq. in.

An error of 0.2 lb. per sq. in. in the pressure produces an error of less than 1 part in 1,000 in the latent heat h_{fg}, and such an error is negligible compared with those already considered. The entire permissible error of 1.7 per cent in q may therefore be borne by the condensate rate, which should be measured to $\pm 2{,}500(0.017) = \pm 42$ lb. per hr. The final recommendations from the principle of equal effects may now be summarized as follows:

Quantity	Allowable Error
Area	±1.7 sq. ft.
Condensate rate	±42 lb. per hr.
Pressure	±0.2 lb. per sq. in.
Terminal water temperature at cold end.	±1.2°F.
Terminal water temperature at hot end.	±0.6°F.

Any one or several of these errors may be increased provided that the increases are offset by corresponding decreases in the others according to (21).

161. Propagation of Errors in Graphical Calculations. Many important design calculations necessitate graphical integrations. For example, one may face the problem of designing a liquid-liquid heat exchanger wherein both the individual film coefficients vary considerably with temperature. The area is calculated by graphical evaluation of the integral

$$A = \int_{\Delta_1}^{\Delta_2} \frac{dq}{U\Delta} \tag{34}$$

where q and Δ are related by a heat balance and U, the over-all coefficient at any point, is a complex function of physical proper-

ties of the liquid, which in turn depend upon the temperature. In this case, a reliable estimate of the error in A due to a given error in the terminal temperatures is best obtained by repetition of the entire calculation, if different values for the terminal temperatures are used. It is especially important to note that, the smaller the temperature difference Δ, the more serious an error of given magnitude in the measured temperatures becomes.

Particularly serious in many calculations on mass-transfer processes are errors in equilibrium data. The common calcula-

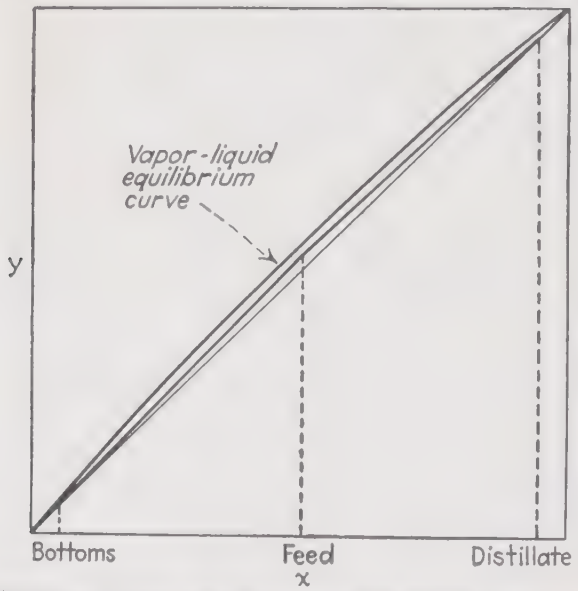

FIG. 113.—McCabe-Thiele diagram for binary system difficultly separable.

tion on a McCabe-Thiele diagram of the number of theoretical plates required to effect a given separation with a given reflux ratio provides an instructive example of the importance of accurate equilibrium data. Figure 113 represents a diagram for a binary mixture of low volatility. A small percentage error in the equilibrium data will cause a large percentage error in the vertical distance between operating line and equilibrium curve with a resultant large percentage error in the number of theoretical plates. The change in the number of theoretical plates due to error in the equilibrium data is best computed by drawing in the equilibrium curve in the position corresponding to the estimated error and repeating the construction for determination

of the number of theoretical plates. A similar procedure should be employed in the estimation of the error produced by equilibrium data in the calculation of number of transfer units in absorption, extraction, or distillation.

162. Special Formulas for Propagation of Errors that Follow the Normal Distribution Law. The chief differences between the errors encountered in practical engineering work and those encountered in the laboratory have been discussed, and it has been pointed out that the formulas of Par. 159 are applicable to any types of errors. In general, the signs of the errors are unknown, but it is probable that in a formula involving several measured quantities some of the errors will be positive and others negative, thus tending to offset each other. When the errors are distributed according to the normal law, special formulas can be derived for the propagation of errors from directly measured quantities to a calculated quantity which take into account the mutual offsetting effect of different errors.

Before discussing the general case, let us consider a quantity M which is a simple linear function of two directly measured quantities M_1 and M_2.

$$M = M_1 + M_2 \tag{35}$$

If q_1 and q_2 are the most probable values of M_1 and M_2, the most probable value of M, denoted by Q, is given by

$$Q = q_1 + q_2$$

As a result of any one set of measurements M_1 and M_2, it is possible to calculate the residuals

$$v_1 = q_1 - M_1 \qquad \text{and} \qquad v_2 = q_2 - M_2$$

and the residual of Q, denoted by E, is given by $Q - M = E$. Combination of these relations makes it clear that

$$E = v_1 + v_2 \tag{36}$$

Squaring (36) gives

$$E^2 = v_1^2 + 2v_1v_2 + v_2^2 \tag{37}$$

Writing (37) for each of n sets of measurements and adding the results, we have

$$\Sigma E^2 = \Sigma v_1^2 + \Sigma 2v_1v_2 + \Sigma v_2^2 \tag{38}$$

Since v_1 and v_2 are distributed in accordance with the three axioms mentioned in Par. 150, their signs will be about equally plus and minus and the terms $2v_1v_2$ will largely offset each other if n is large enough. It is especially important to note that in order for this cancellation to take place v_1 and v_2, and hence M_1 and M_2, must be independent quantities; for if M_1 is a function of M_2 the sign of the residuals will necessarily be related to each other, and the terms will not necessarily cancel.

Dropping $\Sigma 2v_1v_2$ from (37) and dividing through by n, the number of measurements, we have

$$\frac{\Sigma E^2}{n} = \frac{\Sigma v_1^2}{n} + \frac{\Sigma v_2^2}{n} \tag{39}$$

The quantities in this equation are recognized as the squares of the mean square errors (Par. 153); and, since these are proportional to the probable errors and average deviations, (39) can be written in the form

$$\delta^2 = \Delta_1^2 + \Delta_2^2 \tag{40}$$

where δ and Δ represent *any one* of the characteristic errors for calculated and measured quantities, respectively. A similar derivation shows that the same formula would hold if (34) had been written $M = M_1 - M_2$, and if $M = aM_1 + bM_2$ it is easily shown that

$$\delta^2 = (a\Delta_1)^2 + (b\Delta_2)^2 \tag{41}$$

If the functional relation is

$$M = M_1 + M_2 + M_3 \tag{42}$$

we may write

$$M_1 + M_2 = M_s \tag{43}$$

so that $M = M_s + M_3$; then applying (40) results in

$$\delta^2 = \Delta_s^2 + \Delta_3^2 \tag{44}$$

but applying (40) to (43) we have

$$\Delta_s^2 = \Delta_1^2 + \Delta_2^2 \tag{45}$$

and substituting in (44) gives

$$\delta^2 = \Delta_1^2 + \Delta_2^2 + \Delta_3^2 \tag{46}$$

By an obvious extension of the preceding reasoning, it may be shown that if the function takes the general linear form

$$M = aM_1 + bM_2 \cdot \cdot \cdot + nM_n \tag{47}$$

the residual of M takes the form

$$E = av_1 \pm bv_2 \cdot \cdot \cdot \pm nv_n \tag{48}$$

and

$$\delta^2 = a^2\Delta_1^2 + b^2\Delta_2^2 \cdot \cdot \cdot + n^2\Delta_n^2 \tag{49}$$

From (47), it is easy to pass to the general case where

$$M = f(M_1, M_2 \cdot \cdot \cdot M_n) \tag{19}$$

If ΔQ is replaced by δ and the terms Δq by the terms Δ in (21), we obtain

$$\delta = \frac{\partial f}{\partial q_1}\Delta_1 + \frac{\partial f}{\partial q_2}\Delta_2 \cdot \cdot \cdot + \frac{\partial f}{\partial q_n}\Delta_n \tag{50}$$

This is of the form of (48), so that (49) may be applied, with the result that in the case where M_1, M_2 . . . M_n in (19) are *independent* variables

$$\delta^2 = \left(\frac{\partial f}{\partial q_1}\right)^2\Delta_1^2 + \left(\frac{\partial f}{\partial q_2}\right)^2\Delta_2^2 \cdot \cdot \cdot + \left(\frac{\partial f}{\partial q_n}\right)^2\Delta_n^2 \tag{51}$$

Equation (51) is applicable to the two general types of problems considered in Par. 158. Like (21), this equation assumes an especially convenient form when functions such as (24) are dealt with, consisting of the products of quantities raised to powers. In this case, it is convenient to work with either fractional or percentage errors, and by a procedure quite similar to that used to demonstrate (25) it may be shown that the relative error in M in the formula $M = M_1^a M_2^b \cdot \cdot \cdot M_n^n$ is given by

$$\left(\frac{\delta}{Q}\right)^2 = a^2\left(\frac{\Delta_1}{q_1}\right)^2 + b^2\left(\frac{\Delta_2}{q_2}\right)^2 \cdot \cdot \cdot + n^2\left(\frac{\Delta_n}{q_n}\right)^2 \tag{52}$$

The principle of equal effects is applicable to the general formula (51) and the special form (52). In the case of (51), this leads to

$$\delta^2 = n\left(\frac{\partial f}{\partial q_1}\right)^2\Delta_1^2 = n\left(\frac{\partial f}{\partial q_2}\right)^2\Delta_2^2 = \cdot \cdot \cdot n\left(\frac{\partial f}{\partial q_n}\right)^2\Delta_n^2 \tag{53}$$

The use of these formulas will now be illustrated by their application to the solution of the examples solved in Par. 159.

In the previous solution of example 1, it was assumed that the given errors were merely engineering estimates following no particular distribution law. It will now be assumed that the errors given represent average deviations of the mean values of the quantities determined from several independent measurements. Assuming that the average deviations follow the normal law and that (51) is applicable, we have*

$$\left(100\frac{\Delta V_{av}}{V_{av}}\right)^2 = (1)^2\left(100\frac{\Delta W}{W}\right)^2 + (-1)^2\left(100\frac{\Delta\theta}{\theta}\right)^2 + (-2)^2\left(100\frac{\Delta D}{D}\right)^2$$

$$\left(100\frac{\Delta V_{av}}{V_{av}}\right) = \sqrt{1 + (0.7)^2 + 4(1)}$$

$$= \sqrt{5.49} = 2.3\%$$

If the errors had been probable errors or mean square errors, the calculations would have been similar to the one just made as the three characteristic errors are proportional to each other. This result is lower than the 3.7 per cent predicted by formula (25), for the assumed conditions of measurement and types of errors in the two cases are different. The difference between formulas (21) and (51) will be considered further in Par. 163.

In the previous solution of example 2, Par. 160, no attempt was made to allow for the fact that the errors might partly offset each other, the signs of the errors being taken in such a manner that they would affect the error in the coefficient in the same direction. We shall now assume that the errors in the directly measured quantities may be combined according to (51). Assuming equal effects and using the special form (53), we have

$$\left(100\frac{\Delta U}{U}\right)^2 = (5.0)^2 = 3\left(100\frac{\Delta q}{q}\right)^2 = 3\left(100\frac{\Delta A}{A}\right)^2 = 3\left(100\frac{\Delta(\Delta_m)}{\Delta_m}\right)^2$$

* In this formula the special symbol ΔV_{av}, standing for the average deviation of the mean value of V_{av}, replaces the general symbol δ used in Eqs. (39)–(53) to represent any one of the characteristic errors: average deviation, probable error, or mean square error.

When this equation is solved

$$100\frac{\Delta q}{q} = 100\frac{\Delta A}{A} = 100\frac{\Delta(\Delta_m)}{\Delta_m} = \frac{5.0}{\sqrt{3}} = 2.9\%$$

On the basis that

$$\Delta_m = \frac{\Delta_1 - \Delta_2}{\ln \frac{\Delta_1}{\Delta_2}} \tag{30}$$

it might be proposed to place $\Delta_1 - \Delta_2 = a$ and $\ln \Delta_1/\Delta_2 = b$ thus giving $\Delta_m = a\ b$. Assuming equal effects and applying (52) to this fraction would give the equations

$$100\frac{\Delta(\Delta_m)}{\Delta_m} = 2.9 = \sqrt{2\left(100\frac{\Delta_a}{a}\right)^2} = \sqrt{2\left(100\frac{\Delta_b}{b}\right)^2}$$

from which

$$100\frac{\Delta_a}{a} = 100\frac{\Delta_b}{b} = \frac{2.9}{\sqrt{2}} = 2.0\%$$

Since $\Delta_1 - \Delta_2 = 110$, this would indicate an allowable error of 2.2°F. in $\Delta_1 - \Delta_2$; by (53), an allowable error of $2\sqrt{2} = 1.4$°F. in Δ_1 and Δ_2; and again, by (53), an allowable error of

$$\frac{1.4}{\sqrt{2}} = 1\text{°F.}$$

in each terminal temperature. The fallacy in treating the expression for Δ_m in this manner becomes evident upon reference to the derivation in Par. 162 where it was assumed that the errors were independent in order to cause the product terms to offset each other in (38) and similar equations following. Obviously, the error in $a = \Delta_1 - \Delta_2$ is not independent of the error in another function of these same two quantities such as $b = \ln \frac{\Delta_1}{\Delta_2}$. The correct way to treat (30) is to recognize that the independent quantities in this expression are Δ_1 and Δ_2 and apply (53). The required differentiations will proceed as in (31), and we obtain finally

$$\Delta(\Delta_1) = \frac{\Delta(\Delta_m)\left(\ln \frac{\Delta_1}{\Delta_2}\right)^2}{\left[\ln \frac{\Delta_1}{\Delta_2} - \left(1 - \frac{\Delta_2}{\Delta_1}\right)\right]\sqrt{2}} = \pm 5.9\text{°F.}$$

and

$$\Delta(\Delta_2) = \frac{\Delta(\Delta_m)\left(\ln \frac{\Delta_1}{\Delta_2}\right)^2}{\left[-\ln \frac{\Delta_1}{\Delta_2} + \left(\frac{\Delta_1}{\Delta_2} - 1\right)\right]\sqrt{2}} = \pm 2.9°\text{F.}$$

But $\Delta(\Delta_1) = \Delta T_1 - \Delta t_1$ and $\Delta(\Delta_2) = \Delta T_2 - \Delta t_2$ so that the principle of equal effects applied once more in the form of (53) indicates that

$$\Delta T_1 = \Delta t_1 = \pm \frac{5.9}{\sqrt{2}} = \pm 4.2°\text{F.}$$

and

$$\Delta T_2 = \Delta t_2 = \pm \frac{2.9}{\sqrt{2}} = 2.1°\text{F.}$$

The 2.9 per cent error allowable in q will be due principally to the error in the condensate rate W. The allowable error in W then becomes $0.029(2{,}500) = \pm 72$ lb. per hr. As before, an error of 1°F. corresponds to an error of 0.3 lb. per sq. in. in the pressure, and the allowable error in the pressure corresponding to an allowable error of 2.2°F. in steam temperature is $2.2(0.3) = 0.7$ lb. per sq. in. The two different sets of results obtained from using formulas (21) and (51), or their equivalents, are compared in Table XXIV. Since (21) is developed from (20), the equation for total differential of the function, it may be called the "differential formula," whereas (51) which can make allowance for the probable offsetting effects of the various errors will be known as the "probability formula."

TABLE XXIV

Quantity	Allowable error by differential formula	Allowable error by probability formula
Area	± 1.7	± 2.9 sq. ft.
Condensate rate	42	72 lb. per hr.
Pressure	0.4	0.7 lb. per sq. in.
Terminal temperatures:		
Cold end	1.2	4.2
Hot end	0.6	2.1

163. Proper Use of Differential and Probability Formulas. Inspection of Table XXIV indicates a substantial difference

in the allowable error indicated by the two different formulas applied to the same problem, and it is important to understand the conditions under which each of these formulas should be employed. In order to appreciate the differences between the two formulas, it becomes necessary to inquire into the exact meaning of the estimated accuracy of a result. If the true value of a directly measured quantity is represented by M_t and its most probable value by Q, the relation between M_t and Q is given by the equation

$$M_t = Q \pm R \tag{54}$$

where R is a quantity which is given different names by different authors but which will here be known as the "estimated accuracy of the most probable value" Q. If Q is 100 and R is 2, (54) does not mean that the actual error in Q is exactly 2 or that 2 is a more probable error than any other, for if this were so the value of M_t could be computed immediately. Actually a value of 2 for R indicates a belief that in all probability the combined effect of all kinds of errors does not *exceed* ± 2. For a given value of Q, the value of R required to make (54) exactly true is never known and the value of M is never known exactly.

The notation $\pm R$ for estimated accuracy of a result should not be confused with the notation for the quantity known as "probable error," often given as $\pm r$, which indicates that from the standpoint of probability the accidental error of observation is just as likely to be less than r as it is to be greater than r. The errors included in R are not only the accidental errors of measurement, *i.e.*, the precision measure, but also the constant errors that were not removed from the experiment because their removal was either impossible or uneconomic.

We shall now distinguish between two types of measurements. In the first type, the value of Q results from measurements conducted in only one experiment. In so far as is possible, correction is made for all constant errors of known sign and magnitude. There is a limit to the accuracy with which such corrections may be applied, and the errors in the corrections will appear as errors in the final value of Q. The most probable value of the quantity based on the above procedure will then be subject to the unavoidable errors of observation, the errors in the corrections, and constant errors for which no correction

can be made. All of the errors are *estimated* on the basis of past experience and engineering judgment, with the help of special devices such as heat and material balances.

In the second type of measurement, the value of Q results from measurements conducted in several experiments and data are available for calculating probable magnitudes of the accidental errors. As far as it is possible to determine, correction can be made for all constant errors but there will remain errors in the corrections that will partake of the nature of accidental errors. In addition, there are many cases where it is difficult to distinguish between these two types of measurements.

We shall now suppose that it becomes necessary to estimate the accuracy measure of a quantity that is a function of several directly measured quantities. The derived quantity is subject not only to errors in the measured quantities but also to an additional error known as an "error of method" due to some approximation in the function itself. This error will be assumed negligible in the present discussion.

If the values of the quantities concerned come from the second type of measurement, it is almost certain that the accuracy measures of the directly measured quantities will offset each other to a certain extent and allowance for this effect is properly made by combining the accuracy measures by means of the probability formula (51).* It must be remembered, however,

* Formula (51), as derived, related the mean square error of the measured quantities to the mean square error of the derived quantity but was seen to be applicable to the other two characteristic accidental errors, *i.e.*, the probable error, and the average deviation. In the case of a *direct* observation on a quantity of most probable value Q

$$Q = Q' + C_1 + C_2 \cdot \cdot \cdot + C_n \tag{55}$$

where Q' is the mean of the observations and the quantities C are known corrections for constant errors. The combined effect of all the errors is the accuracy measure denoted by R in (54). On the assumption that the errors in the corrections behave as accidental errors, these errors, denoted by ΔC_1, ΔC_2 . . . ΔC_n, may be combined with the accidental error of observation in Q' by means of (51).

The accidental errors and the errors in the corrections should theoretically be expressed in terms of the same characteristic error; *i.e.*, all should be either average deviations, or probable errors, or mean square errors (see Par. 153). Practically, there is very little numerical difference among the three characteristic accidental errors. If $\Delta Q'$ represents any one of the

that the disappearance of the cross-product terms which allows for the offsetting effect of the various accuracy measures is complete only when there is a large number of measurements.

On the other hand, if the values of the quantities concerned come from the first type of measurement and the magnitudes of the various accuracy measures are based, not on a series of observations, but on estimates alone, the most conservative practice would be to compute the probable maximum error in the derived quantity by means of the differential formula, arbitrarily assigning such signs to the individual accuracy measures that they will all act to increase the value of R in (54). This will naturally indicate a larger value for the accuracy measure of the result than would be obtained by applying the probability formula.

The previous discussion applies also to the problem of estimating the allowable accuracy measures of the directly measured quantities, given the desired accuracy measure of the calculated quantity. The same two cases must be distinguished, except that in this case we are discussing measurements to be made in the future. Table XXIV indicates the liberality of the probability formula compared with the differential formula.

164. Discussion of Completed Measurements. A Summary. The result of an investigation should always be accompanied by a suitable discussion of its reliability, and we shall summarize the procedure to be followed in the case of direct and indirect measurements.

Direct Measurements. In the case of a direct measurement, it is not sufficient to report the mean of a series of observations, for this is a measure only of the agreement of the measurements among themselves, *i.e.*, the precision of the measurements, and indicates nothing with respect to the presence and magnitude of any constant errors. Careful consideration must be given

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characteristic errors of observation, such as the average deviation, and ΔC_1, ΔC_2 . . . ΔC_n are corresponding errors in the corrections, the accuracy measure of the directly measured quantity is then obtained from the equation

$$R^2 = (\Delta Q')^2 + (\Delta C_1)^2 + (\Delta C_2)^2 \cdots + (\Delta C_n)^2 \qquad (56)$$

It is easily shown that the accuracy measures of the directly measured quantities may be combined by (51) to give the accuracy measure of the derived quantity, provided that the accuracy measures follow the axioms of accidental error.

to all types of constant errors and corrections made if possible When possible, corrections are calculated, but very often they are made by means of calibrations of the measuring instruments under carefully controlled conditions. The errors in the corrections and the accidental errors may be combined according to Eq. (51), provided that sufficient measurements have been made to justify application of the theory of least squares. When the presence of indeterminate constant errors is suspected, the magnitude of these should be estimated, but the method of estimation to be employed will vary with the situation.

If an indeterminate error is suspected as being seriously large, the preferable method of determining its magnitude is to perform the measurement by independent methods and compare different results. In this connection, it should be emphasized again that the method employed in Par. 155 for combining the mean values of measurements of the same quantity performed by different methods assumes that all errors involved in the estimates of accuracy follow the normal distribution law and should not be used for combining measurements the errors in which do not conform to the normal law. In the comparison of two measurements made by different methods for the purpose of estimating the magnitude of a constant error, the most conservative practice is to report the deviations of the measurements from each other and indicate this as a measure of the constant error. If this estimated value of the constant error is considered together with the errors in the corrections for determinate and accidental errors, one will have a good picture of the reliability of a direct measurement. If these three types of errors are to be combined to give an over-all estimate of maximum probable error, the most conservative practice would be to give this estimate as the sum of their absolute values. A more liberal procedure would consist in making allowance for offsetting effects of the different errors, but, in general (except when all of the errors follow the normal law or some other known law), any allowance of this type is arbitrary.

Indirect Measurements. A measure of the error in each of the direct measurements having been obtained, it next becomes necessary to combine these to determine the error in the result calculated from the best values of the directly measured quantities. The various methods of accomplishing this and their

limitations are fully reviewed in Par. 163. The error in the calculated result is now considered in connection with the error of method (Par. 144), and again the most conservative practice is to report the sum of the absolute values of these two errors as the probable maximum value of the error in the indirectly measured quantity. Not infrequently, when accurate results are necessary the procedure involved in arriving at an estimate of the reliability of the result will occupy a longer time than the final measurements themselves.

Discussion of Proposed Measurements. All measurements represent expense, and only by careful planning and preliminary discussion can a measurement be executed with the desired degree of accuracy and the greatest degree of economy. In general, the accuracy sought should be consistent with the purpose for which the results are to be employed, but if it is possible to obtain better than minimum allowable accuracy at no additional expense this should always be done on the theory that the more accurate results may be of value for purposes unforeseen at the time of original measurement.

The desired accuracy in the result having been agreed upon, the problem is one of determining the allowable errors in the various measurements. The procedure here follows Par. 160 or 162. When these allowable errors are determined, it is necessary to ascertain whether or not they will be exceeded by the proposed methods of measurement. Before this question can be answered, it may become necessary to perform some preliminary observations. For example, in the case of a chemical analysis, the error may be ascertained by testing out the method on a sample of known composition. Preliminary measurements consume time, but it is far less expensive to discover by this means that a proposed method must be modified, than to be forced to repeat the final measurements.

Quite frequently, the accuracy of an indirectly measured quantity being measured by a given method may be improved by proper selection of the magnitudes of the directly measured quantities that are concerned. An example of this nature occurs in the measurement of certain absorption coefficients. In the absorption of CO_2 in water in a countercurrent packed tower, the higher the tower, the nearer the approach to equilibrium of the gas entering and the liquid leaving, and the nearer the

approach to equilibrium, the smaller the driving force for absorption. The percentage error in the analysis of a CO_2 solution increases as the solution becomes more dilute, and this tends to throw off the material balance on the tower. On the other hand, even though a fairly concentrated CO_2 solution could be analyzed with a small percentage error, this small error might lead to a huge error in the driving force, which becomes a small difference between two numbers (see Par. 146) as the concentration of CO_2 in the liquid increases toward its equilibrium value determined by CO_2 concentration in the gas. Clearly, under such circumstances, it is possible to select operating conditions such that the combined effect on the calculated absorption coefficient of the errors in the driving force and the errors in the analysis is a minimum.

When it becomes evident that the required accuracy cannot be obtained by any practical adjustment of the allowable errors in the directly measured quantities, it is necessary either to accept a lower order of accuracy or to adopt a different scheme of measurement.

APPENDIX

EXAMPLES

1. In the design of a certain piece of equipment, it is found that the two costs involved may each be expressed as a power function of a design variable x.

$$\text{Total costs} = A + B$$

where $A = ax^n$

$B = bx^{-m}$

Show that for the optimum design, *i.e.*, the value of x corresponding to minimum total cost, the ratio of the individual costs A and B is m/n.

2. Derive the expressions given in Par. 9 for the interstage pressures corresponding to minimum total work for the three-stage polytropic compression of a perfect gas. What would be the optimum interstage pressure p_2 for the two-stage compression from p_1 to p_3 if half of the original gas were withdrawn at p_2 and not compressed to p_3? In each case, the gas is cooled to the original temperature after each stage.

3. The porosity of acid carboy stoppers was determined experimentally by measuring the volume of air at atmospheric conditions passing through the stoppers at constant pressure. The flow of air through one stopper tested may be expressed by the relation

$$R = 0.0030P^{1.13}$$

where R represents cubic feet per minute of air at atmospheric (70°F., 1 atm.) conditions and P represents the gauge pressure, pounds per square inch.

A standard type of tester consists of a tank with an opening, into which the stopper may be placed, and an air supply line. The porosity of the stopper is measured in this type of apparatus by observing the time required for the pressure to drop from 20 to 5 lb. per sq. in. gauge. What would be the time required for this pressure drop in the case of the stopper mentioned if the volume of the tank is 2.09 cu. ft.? Assume that the expansion is isothermal. Repeat on the assumption that expansion is adiabatic.

4. Three tanks of 10,000-gal. capacity each are arranged so that when water is fed into the first an equal quantity of solution overflows from the first to the second tank, likewise from the second to the third, and likewise from the third to some point out of the system. Agitators keep the contents of each tank uniform in concentration. To start, let each of the tanks be full of a solution of concentration "C_0" lb. per gal. Run water into the first tank at 50 gal. per min., and let the overflows function as described above.

How long will be required to reduce the concentration in the first tank to C_a 10? What will be the concentrations in the other two tanks at this time?

5. A copper plate $\frac{1}{4}$ in. thick is in contact with a current of air flowing parallel to one surface. The other surface of the plate is well insulated. The temperature of the air stream varies in a regular fashion as given by the relation

$$t = 300 + 200 \sin \pi\theta$$

where t is the air temperature, °F., and θ represents time, hours. Neglecting the temperature gradient in the plate, calculate (1) the time interval between the instant the air cools to 300° and the instant the plate is next at 300° and (2) the maximum temperature of the plate.

Assume that the process has been in operation for a considerable period of time, so that each cycle is identical with that preceding. The plate has a density of 552 lb. per cu. ft. and a specific heat of 0.111. The surface coefficient of heat transfer from air to plate is 4.0 B.t.u. (hr.)(sq. ft.)(°F.).

6. In a shell-and-tube-type heat exchanger the cold liquid enters at one end, makes one pass, reverses in direction, and leaves from the same end at which it enters. The hot liquid enters at the opposite end and flows through in one pass. Considering the temperature of the hot liquid uniform over any cross section and neglecting variations in the over-all coefficient of heat transfer from hot to cold liquid, derive an expression for the true average temperature difference in such an exchanger in terms of the terminal temperatures of the flowing fluids.

NOTE: Consider a differential cross section of exchanger, set up the proper heat balances and rate equations, and integrate the resulting set of simultaneous differential equations.

7. In an experimental study of the saponification of methyl acetate by sodium hydroxide, it is found that 25 per cent of the ester is converted to alcohol in 12 min. when the initial concentrations of both ester and caustic are 0.01 molal. What conversion of ester would be obtained in 1 hr. if the initial ester concentration were 0.025 molal and the initial caustic concentration 0.015 molal?

8. Bodenstein* reports the following data on the dissociation of HI at constant volume at the boiling point of sulfur:

Min.	10	20	30	40	50	60
Fraction HI dissociated	0.084	0.0917	0.1315	0.1571	0.1771	0.1878

Min.	70	80	Equilibrium
Fraction HI dissociated	0.1963	0.2043	0.2143

Test the applicability of the second-order equation by plotting the data, using coordinates such that a straight line should result if the reaction is second order.

* *Ber.*, **26**, 2609 (1893).

Calculate the average reaction-rate constant in the units of minutes and mol fractions.

9. A refractory tube 200 cm. long, 2.0 cm. i.d., is supplied with pure N_2O at 1 atm. and at 757°C. The average gas velocity at the gas inlet is 2.0 cm. per sec., and the tube is maintained at a constant temperature of 757°C. Using a reaction-rate constant obtained from Par. 34, determine the composition of the gas leaving the tube.

10. Daniels and Johnston* report the following data on the thermal decomposition of N_2O_5 at constant volume at 55°C:

Time (min.)	Total pressure (mm. Hg)	Time (min.)	Total pressure (mm. Hg)
0	331.2	14	589.4
3	424.5	16	604.0
4	449.0	18	616.3
6	491.8	22	634.0
8	524.8	26	646.0
10	551.3	Infinite	673.7

The reaction is

$$2N_2O_5 = 2N_2O_4 + O_2$$

but the tetroxide dissociates to form NO_2, with which it is in constant equilibrium. The main reaction has been shown to be not reversible, and the N_2O_5 has been shown to exist as such, and not as a polymer.

Making due allowance for the equilibrium between N_2O_4 and NO_2, determine the order of the reaction (test two possibilities) by plotting the data in such a way as to obtain a straight line for the correct mechanism.

11. The dried gas from an ammonia oxidation catalyst chamber contains 9 per cent NO, 9 per cent oxygen, and 82 per cent nitrogen (by volume). This gas is passed at 25°C. and 1 atm. into a vertical wetted-wall absorption column, the walls of which are wet with a dilute solution of sodium hydroxide. The tower is 200 cm. tall, 5 cm. i. d., and the inlet gas velocity is 97.1 cm. per sec. What is the percentage recovery of nitrogen oxides in the column?

For purposes of calculation the following assumptions may be made. (1) The concentrations at any point will be based on the total mols taken as constant and equal to the arithmetic mean of initial value and the final value corresponding to complete absorption. (2) The NO_2 concentrations will be so low that N_2O_4 formation may be neglected. (3) The NO is not absorbed. (4) The NO_2 is absorbed as such, with gas film controlling and no partial pressure of NO_2 over the solution. The absorption coefficient k_G is 3.1×10^{-7} g. mols/(sec.)(sq. cm.)(mm. Hg.).† Bodenstein gives the reaction-rate constant for the oxidation of NO at 25°C. as $k = 1.77 \times 10^{12}$

* *J. Am. Chem. Soc.*, **43**, 62 (1929).

† See Chambers and Sherwood, *Ind. Eng. Chem.*, **29**, 1415 (1937).

(g. mol)²/(cu. cm.)²(min.), and shows that the reaction is homogeneous and third order. The rate equation is

$$+\frac{d[NO_2]}{d\theta} = k[NO]^2[O_2]$$

12. A simple adiabatic converter for the oxidation of SO_2 to SO_3 is to operate upon raw gas entering at 400°C. and 1.70 ft. per sec. and containing 0.60 per cent SO_3, 10.1 per cent SO_2, 10.0 per cent O_2, and 79.3 per cent N_2. Using the following data, estimate the thickness of catalyst mass necessary to convert 57.0 per cent of the entering SO_2 to SO_3. Pressure = 1 atm.

Under these conditions for the catalyst mass being used, the net rate of oxidation of SO_2 may be calculated from the equation*

$$-\frac{dx}{d\theta} = k\frac{x^2}{(y)^{0.2}}\ln\frac{r_e}{r}$$

y = mols SO_3 at time θ per 100 mols entering gas.
x = mols SO_2 at time θ per 100 mols entering gas.
θ = time of contact, sec. (based on catalyst bulk volume and superficial gas velocity).
T = temperature of gas after time of contact θ.
r_e = molal ratio of SO_3 to SO_2 at equilibrium at temperature T.
r = molal ratio of SO_3 to SO_2 at time θ.
k = reaction-rate constant at temperature T.
K = equilibrium constant = $p_{SO_3}/p_{SO_2}\sqrt{p_{O_2}}$, ($p$ in atm).

T (°C)	400	425	450	475	500
k	6.6	13.6	5.2	2.7	2.0

$$RT \ln K = 22{,}600 - 21.36T, \quad T \text{ in °K.}$$

$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$; $\Delta H = -22{,}600$ g. cal./g. mol (constant and independent of temperature)

The following heat capacities may be considered constant over the range involved:

MCp for N_2 = 6.8 g. cal./(g. mol)(°C.)
MCp for O_2 = 6.8 g. cal./(g. mol)(°C.)
MCp for SO_2 = 11.0 g. cal./(g. mol)(°C.)
MCp for SO_3 = 14.4 g. cal./(g. mol)(°C.)

13. Solve the following ordinary differential equations:

1. $(y - x)dy + y\,dx = 0$
2. $(y^3 - 2x^2y)dx + (2xy^2 - x^3)dy = 0$
3. $(y + x)dx + x\,dy = 0$
4. $(2y + 3xy^2)dx + (x + 2x^2y)dy = 0$

* Chang and Chang, *J. Chem. Eng. (China)*, Vol. 3, No. 4, p. 315 (1936).

5. $\dfrac{dy}{dx} - \dfrac{y+1}{x+1} = \sqrt{y+1}$

6. $(2x^3y^2 - y)dx + (2x^2y^3 - x)dy = 0$

7. $x(1+x^2)\dfrac{dy}{dx} + 4x^2y = 2$

8. $(xy^2 + y)dx - x\,dy = 0$

9. $x\,dy + (y - y^2 \ln x)dx = 0$

10. $\left(2x\dfrac{dy}{dx} - y\right)^2 = 8x^3$

11. $xy^2\left(\dfrac{dy}{dx}\right)^2 - y^3\dfrac{dy}{dx} + x = 0$

12. $\dfrac{d^3y}{dx^3} - \dfrac{dy}{dx} = 0$

13. $\dfrac{d^4y}{dx^4} + 2\dfrac{d^2y}{dx^2} + y = 0$

14. $y\dfrac{d^2y}{dx^2} + 2\dfrac{dy}{dx} - \left(\dfrac{dy}{dx}\right)^2 = 0$

15. $\dfrac{d^2y}{dx^2} + x\dfrac{dy}{dx} = x$

14. Compute an integral curve through the point $x = 1.0$, $y = 3.0$ and over the range ($x = 1.0$, to $x = 4.0$) for the equation

$$\frac{dy}{dx} = 0.1(y + x)^{0.8}$$

15. Compute an integral curve passing through the point ($x = 1.0$; $y = 4.0$), with a slope of $\frac{1}{2}$ at this point and over the range ($x = 1.0$ to $x = 4.0$) for the equation

$$\frac{d^2y}{dx^2} = y^2 + xy + x^2$$

16. Transform the basic heat-conduction equation (16) of Par. 98 into spherical coordinates. In this coordinate system, a point P is located by its distance p from the origin O and by two angles θ and ϕ. θ represents the angle between OP and the x-y plane, and ϕ represents the angle between OP and the x-z plane.

17. Derive an expression for the rate at which the free energy F changes with the pressure at constant entropy. This expression is to contain derivatives having either p or T as the independent variable, as well as the necessary fundamental quantities. Note that the resulting expression contains S. Would it be possible to obtain an expression for $\left(\dfrac{\partial F}{\partial P}\right)_S$ not containing S, no restriction being placed on the derivatives employed?

18. Obtain an equation expressing the rate at which free energy varies with energy in a constant-volume process. The equation is to contain the necessary fundamental quantities but only p and T as independent variables in the derivatives.

19. Obtain a solution in power series for

$$\frac{dy}{dx} = x + y^2 + 1$$

where $y = 0$ at $x = 0$. Evaluate the coefficients of the terms up to x^6. Note that the nature of the series cannot be determined from the first four terms alone. Compare the result with that obtained by solution in Taylor's series. Calculate the value of y at $x = -1$, and note that the series converges rapidly only when x is a fraction.

20. Solve the equation

$$(x + y)dx + (x + y + 1)dy = 0$$

by ordinary integration and by solution in power series.

21. A metal plate has a width π and is infinite in length. The two edges are maintained at a constant temperature of zero, and the end at a constant temperature unity. Obtain an expression for the temperature as a function of the position in the plate.

22. A large slab of steel, 1 ft. thick, has one face at 700° and one face at 400°F. The central plane is at 400°, and the temperature distribution in each half is linear. While in this condition the slab is suddenly quenched so that the faces are maintained at 100°F. Determine the temperature at the central plane after 15 min. by (1) the analytical method and (2) the graphical method. The steel has a thermal conductivity of 25 (B.t.u.)(ft.)/(hr.)(sq. ft.)(°F.), a density of 490 lb./cu. ft., and a specific heat 0.130.

23. Repeat the graphical solution to Prob. 22, assuming the steel to be initially at a uniform temperature of 700°F. and to be cooled in oil at 100°F., the surface coefficient of heat transfer from steel to oil being 120 B.t.u./(hr.)(sq. ft.)(°F.).

24. The relation between moisture concentration, time, and position for the constant-rate drying of an infinite slab was obtained as Eq. (86) of Par. 103. Check this result by differentiation to see if it is compatible with the original differential equation and with the three boundary conditions.

25. Tests on a high-pressure gas cooler give the following data relating the over-all coefficient of heat transfer U and the mass velocity G of the gas passing through the tubes:

U	3.1	6.0	11.2	14.8	20
G	0.5	1.0	2.0	3.0	5.0

Using the method of least squares, obtain the parabola of the form

$$U = a + bG + cG^2$$

that best fits the data. Would the resulting form be suitable for extrapolation to higher values of G? Can you suggest a simple empirical equation that would fit the data as well and be of a more suitable form?

26. Air at 70°F. and 2 atm. total pressure is flowing through a round duct 18 in. in diameter. The rate of flow is to be measured by three Pitot tubes spaced across one duct diameter at the proper positions to enable the Gauss method of integration to be employed in calculating the total air flow. What are the correct positions for the three tubes? After spacing the tubes correctly, it is found that the manometer reading for the middle one is 0.01 in. water, and the readings for the other two are 0.007 and 0.005 in. water, respectively. What is the total air flow, expressed as cubic feet per second at 70°F. and 1 atm.?

27. The velocity V_2 through a sharp-edged orifice of diameter D_2 is given by the expression

$$\sqrt{V_2^2 - V_1^2} = C\sqrt{2gh}$$

where V_1 is the velocity in the approach pipe and h is the manometer reading. The orifice coefficient C is expressed graphically as a function of the Reynolds number $D_2V_2\rho/\mu$ and the ratio D_2/D_1. Here ρ represents the density and μ the viscosity of the fluid flowing, and D_1 is the diameter of the approach pipe.

In the usual calculation of the rate of flow corresponding to a given manometer reading, a trial-and-error calculation is encountered. How might the correlation of data on orifice coefficients be replotted to obviate trial and error in this type of calculation?

28. Obtain from the "International Critical Tables," or other sources, data on the viscosity-temperature relations for water, mercury, several organic liquids, and several hydrocarbon oils. Prepare a graph of the "Cox-chart" type with an arbitrary temperature-ordinate scale and a logarithmic viscosity-abscissa scale. Base the ordinate scale on a straight line chosen to represent the data for one of the light oils. Having prepared this scale, plot the other data and note the degree to which the results approximate straight lines.

29. As wet peat is dried, its volume shrinks to as little as 30 per cent of its original wet volume. Most of the water vaporizes at a constant rate expressed as grams per hour per square centimeter of exposed surface.

A peat sample is dried, and data are collected on the relation between time and moisture content. Shrinkage is such that any linear dimension may be expressed as

$$L = L_0(1 + CW)$$

where L_0 is the corresponding dimension of the dry peat, W is the water content as grams water per gram dry peat, and C is an unknown constant. Obtain a relation between W and time for the "constant-rate" period, and show how the experimental data should be plotted to test the resulting equation.

30. A solution of acetic acid and benzene containing 60 per cent acetic acid by weight is extracted with water at 25°C. One hundred pounds of the original solution is treated first with 50 lb. water, and after agitation the two layers are separated. The water layer is treated with a second 50 lb.

of water and the phases again separated. What percentage of the acetic acid in the original solution is obtained in the final aqueous solution?

Data on benzene, water, acetic acid at 25°C.*:

Upper layer			Lower layer		
Acid	Benzene	Water	Acid	Benzene	Water
0.46	99.52	0.02	9.4	0.18	90.42
1.30	98.64	0.06	16.5	0.31	83.19
3.1	96.75	0.15	28.2	0.53	71.27
5.2	94.55	0.25	37.7	0.84	61.46
7.0	92.66	0.34	43.9	1.5	54.6
8.7	90.88	0.42	48.3	1.82	49.88
10.5	88.99	0.51	53.2	2.72	44.08
16.3	82.91	0.79	61.4	6.1	32.5
21.5	77.46	1.04	64.5	9.2	26.3
30.5	67.37	2.13	66.0	13.8	20.2
32.8	64.76	2.44	65.0	17.8	17.2
46.5	47.9	5.7	60.0	29.0	11.0
52.8	39.6	7.6	52.8	39.6	7.6

What percentage recovery of acetic acid in the water layer is possible when the same total amount of water (100 lb.) is used in a two-stage batch countercurrent process?

31. A small laboratory rectifying unit consists of a still, a very efficient column containing the equivalent of 30 perfect plates, a condenser, and a condensate reservoir. The condensate reservoir is connected to the column so that condensate may be returned as reflux. Three gram mols of a binary mixture containing initially 60 per cent A and 40 per cent B are charged to the still and distilled with a reflux ratio of 9 mols of reflux to 10 mols of vapor entering the condenser. The condensate not returned to the column is allowed to collect in the condensate reservoir. Condensate entering the condensate reservoir mixes uniformly with the contents of the reservoir, and reflux is drawn directly from the reservoir. B is the low-boiling component, and the relative volatility of B to A (see page 35) is 2.3. Assuming negligible holdup in the column, prepare a graph of composition of liquid in condensate reservoir versus the mols of liquid in the reservoir covering the range 0 to 1.0 mol. (Initial compositions are given as mol per cent.)

32. Each of the following quantities is in error to the extent indicated.

$a = 5.20 \pm 0.02$ $\qquad x = 15{,}400 \pm 200$

$b = 0.00175 \pm 0.00003$ $\qquad y = (5.33 \pm 0.03)10^4$

$c = 75 \pm 2$ $\qquad z = 4.98 \pm 0.03$

Determine the maximum values of the absolute and relative errors in the quantities resulting from performance of the following operations:

* WADDELL, *J. Phys. Chem.*, **2**, 233 (1898).

(1) $a + b + x + y$
(2) $a + b - z$
(3) $y^{3.2}$
(4) $\log (a - z)$
(5) antilog $(a - z)$
(6) $\frac{x}{y}$
(7) abc
(8) $\int_{W=z}^{W=c} \frac{dw}{w - a}$
(9) $\int_{w=z}^{w=c} \frac{dw}{a - \ln w}$
(10) $a + z = p$ Find error in solution for p and q.
$a - z = q$
(11) $p^2 + ap + z = 0$ Find error in solution for p.

33. Repeat Prob. 32 on the assumption that the indicated errors in the quantities are average deviations and that the principle of least squares may be applied.

34. In the calculation of a heat-transfer coefficient from several sets of data, the following results were obtained:

40 ± 3 B.t.u./(hr.)(sq. ft.)(°F.)
38 ± 5
42 ± 6
41 ± 2

On the basis of these values, what is the best value for the coefficient? What can be stated with regard to (1) the precision, and (2) the accuracy of this value?

35. The volume of stack gas leaving an oil-fired boiler is to be calculated from the Orsat analysis of the gas, the analysis of the oil fired, and the rate of firing. Approximate values of these quantities are

Orsat Analysis		Temperature of flue gas	430°F.
CO_2	11.1%	Temperature of air	80°F.
O_2	5.3%	Humidity of air	Unknown
CO	0.2%	Oil:	Per cent C = 85.7%
N_2	83.4%	Percentage O	(negligible)
Oil rate	105 gal./hr.	Barometer	758 mm. Hg.
Specific gravity of oil = 0.90		Pressure of stack gas = 5 in. H_2O	

How accurately must each of the quantities be measured if the volume of stack gas is desired accurate to 5.0 per cent. On the assumption that the partial pressure of water vapor in the entering air is 3.0 ± 0.2 mm. Hg and if the tolerances just calculated are used, what is the accuracy in the calculated value for partial pressure of water in the stack gases?

36. A binary mixture of two completely miscible components obeying Raoult's law has a relative volatility of approximately 1.25. The original mixture containing 60 mol per cent A (low boiler) is to be rectified to an overhead product of 98 mol per cent A and a bottoms of 98 mol per cent B. The feed will enter at its boiling point, and the ratio of reflux to overhead product will be 2.30. How accurately must the relative volatility be known to ensure that the number of calculated perfect plates required be accurate to 10 per cent?

37. In a control test a sample of basic solution containing approximately 2.00 milliequivalents of base is titrated with standard acid. The normality of the standard acid can be measured to ±0.001 and the volume of acid to ±0.05 cc. What acid normality and volume should be used under these

circumstances to assure minimum error in the determination of the number of basic milliequivalents, and what will this error be?

1. Assume applicability of the differential formula.
2. Assume applicability of the probability formula.

38. An experimental heat exchanger to heat a mixture of N_2O_4 and NO_2 vapor is to consist of a 1 in. i.d. stainless-steel tube jacketed by a 2 in. i.d. ordinary-steel tube. Hot water at 180°F. will enter the space between the two tubes at the rate of 10.5 gal. per min. and flow countercurrent to the gas mixture. In the preliminary design of the exchanger, it is desired to calculate the necessary length to heat the gas mixture from 80 to 150°F. if no lagging is used on the outside. The gas mixture enters at 2 atm. and is equivalent to 90 lb. per hr. of N_2O_4. The temperature of the surroundings will be taken as 70°F.; and the over-all coefficient for heat transfer from pipe surface to surroundings by radiation, conduction, and convection is designated as $(h_c + h_r)$ B.t.u./(hr.)(sq. ft.)(°F.) and may be calculated from the equation $(h_c + h_r) = 2(10)^{0.00095\Delta T}$, ΔT being temperature difference between pipe surface and surroundings in degrees Fahrenheit. The water-film coefficients are given by

$$h_w = \frac{160(1 + 0.01t)V^{0.8}}{(D')^{0.2}}$$

t = water temperature, °F.; V_s = average water velocity, ft. per sec.; D' = hydraulic radius, in. = cross-sectional area/wetted perimeter.

The gas-film coefficient is given by

$$h_g = \frac{0.0144CpG^{0.8}}{D^{0.2}}$$

Cp = apparent heat capacity B.t.u. (lb.)(°F.) of NO_2-N_2O_4 mixture at constant pressure; G = mass velocity, lb./(hr.)(sq. ft.); D = tube diameter, ft.

At all points in the exchanger, it may be assumed that equilibrium prevails for the reaction $N_2O_4 \rightleftarrows 2NO_2$, and the equilibrium constant

$$Kp = \frac{p^2_{NO_2}}{P_{N_2O_4}}$$

is given as a function of temperature by the equation

$$\ln Kp = \frac{-7030}{T} + 21.58$$

where T is in degrees Kelvin and Kp is for pressures in atmospheres. Heat of dissociation of N_2O_4 is 13,900 g. cal per g. mol and undergoes only slight variation over the range involved. Heat capacity of NO_2 has an average value of 8.80 B.t.u./(lb. mol)(°F.) over this range whereas the heat capacity of N_2O_4 varies as shown in the following table:

T (°F.)	92.6	108.5	136.5	152.6	176.0	207.5
MCp for N_2O_4 B.t.u./(lb. mol)(°F.)	11.4	12.0	14.9	15.7	16.1	17.5

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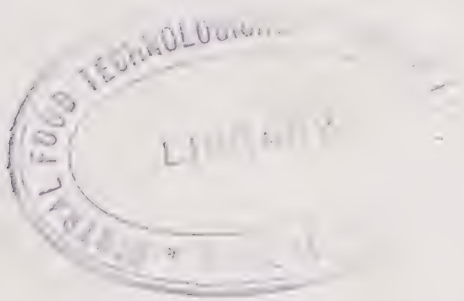

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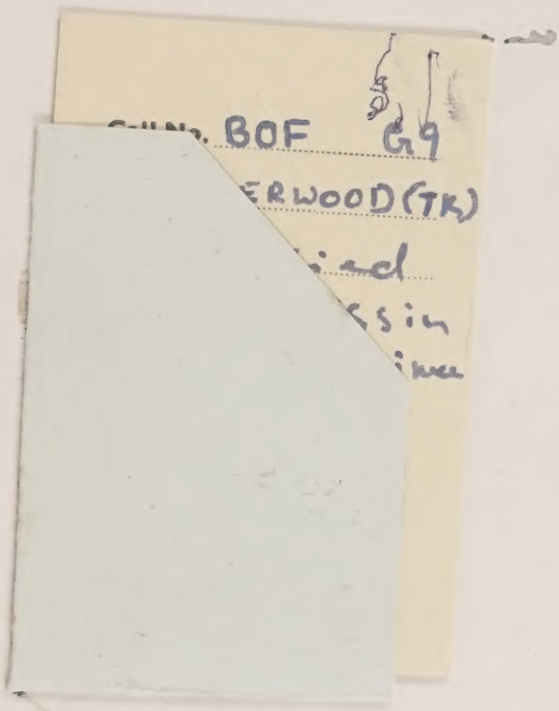
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